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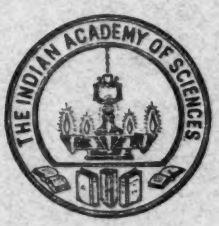

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LIGHT-SCATTERING, RAMAN SPECTRA AND ALLIED PHYSICAL PROPERTIES OF SOME ESSENTIAL AND VEGETABLE OILS.

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1. *Introduction.*

Extensive investigations on the intensity of scattered radiation in many liquids were made by Martin, Raman and Rao, Cabannes, Krishnan and others. A detailed and connected discussion of these data has been given by Cabannes (1929). Such observations were recently extended from pure liquids to some Indian vegetable oils in this laboratory by Jogarao (1936). In a few cases, he has shown that there is satisfactory agreement between the observed and calculated values of the intensity of the scattered radiation, thus supporting the statement that the scattering in vegetable oils investigated is also of molecular origin. He could not however calculate the intensities in some cases due to lack of data regarding compressibilities. Even in such cases, namely olive and castor oils, where calculations could be made, it is not known if the compressibilities adopted are isothermal or adiabatic. One of the aims of the present investigation is to obtain the compressibilities of all these oils under reliable and known conditions with a view to check the figures relating to the intensity of scattered light.

Moreover, different investigators in this field have gathered most of the data necessary for purposes of calculation from diverse authors and no one has systematically determined the values of the various parameters that fall in the equation for the intensity of the scattered light. From this point of view, the present investigation may also be regarded as a systematic and complete study of all the required properties, namely, the adiabatic compressibility, rate of variation of specific volume with temperature, specific heat at constant pressure, depolarisation factor and intensity of the scattered radiation for a number of essential oils and a few easily available Indian oils. With the data thus gathered the isothermal compressibility is easily calculated from thermodynamical relations. These figures permit us to calculate the intensity of the scattered radiation and the results are compared with the

observed values. In addition to these, the optical rotation of the plane of polarisation also is measured. With a view to throw light on the chemical constitution of the chief constituents of the essential oils the Raman spectra of some of them are also taken.

2. *Oils used and Their Purification.*

Essential oils.—Many essential oils are mixtures and the chief constituents are usually volatile. They can easily be distilled under reduced pressure or a current of steam. It is well known that the composition of these essential oils is not only most complex but also subject to variation from sample to sample. In spite of this complexity, the majority of the essential oils owe their characteristics to one or more chief constituents which are generally known. The present investigation aims at throwing light on the nature and physical properties of these chief constituents. In the following table the essential oils studied are given along with their chief constituents.

TABLE I.

Essential Oils investigated and their Chief Constituents.

Name of the oil	Chief constituent and its composition
Eucalyptus oil	Cineole $C_{10}H_{18}O$
Cajeputi oil	Cineole ,,
Coriandri oil	Dextro Linalol ,,
Anisi oil	Anethole $C_{10}H_{12}O$
Citronellæ oil	Geranial $C_{10}H_{17}OH$
Santali oil	Santalol $C_{15}H_{26}O$

All the above oils with the exception of citronellæ oil are samples obtained from Merck and are of a high degree of purity. They have been distilled twice under reduced pressure and the distillate in all cases is quite colourless and absolutely dust-free. Citronellæ is of a different make and has been purchased locally. This has been distilled thrice but a slight yellow colour persisted. In all the investigations described below, oils purified in the above manner have been used. In the case of compressibility measurements it is thought that prior distillation is unnecessary as preliminary experiments in the case of coriandri showed that distillation has no effect on the results.

Vegetable oils.—Three Indian vegetable oils, namely, cocoanut oil, groundnut oil and castor oil, have been studied. Extra pure and triple refined samples of castor oil and cocoanut oil are available and hence no further purification is made in these cases. Groundnut oil decolourised and centrifuged in this laboratory in another connection is taken.

3. *Compressibilities : Isothermal and Adiabatic.*

Of the various physical properties that affect the molecular scattering of light in liquids, the isothermal compressibility is a very important one. The so-called isothermal values of the early investigators are not without errors due to the various difficulties that creep in the process of measurement. As Tyrer (1913 & 14) pointed out, no two earlier investigators agree in their values, specially under low pressures, where the processes are not strictly isothermal as they thought them to be. At low pressures, say within an atmosphere, there occurs a small rise in temperature amounting to a few thousandths of a degree yet sufficient if neglected to cause a difference of 10 to 40 per cent. in the observed isothermal compressibility. The elimination of the rise in temperature is exceedingly difficult due to the insensitivity of the thermometers. Hence their values are somewhere between isothermal and adiabatic. The later work of Tyrer (1914) with his two types of piezometers of soft glass and copper is very thorough and accurate. He determined the compressibilities after eliminating the various errors. In the present paper, a similar piezometer has been used for the measurement of the adiabatic compressibilities.

Description of the piezometer.—The piezometer constructed by the author slightly differs from that of Tyrer's in its details. All the parts of the piezometer (Fig. 1) are made up of soft glass.

A is the internal vessel for liquid resting on a properly cut cork *W* at the bottom of the concentric outer jacket *F*. The vessel is exhausted through the side tube *D* before the liquid is admitted to fill it completely through the funnel *E*. On filling the liquid completely up to the taps T_1 and T_2 care is taken to see that no air bubbles stick within. The few that remain in, in the case of viscous liquids like castor oil, santali, etc., are removed by slightly heating the parts and properly tilting the apparatus. Closing the taps T_1 and T_2 the bent arm *B* is slightly heated so that the liquid expands through the capillary *C*. A dry mercury pellet is introduced through the tap T_3 and the apparatus is inclined such that the pellet is taken into the capillary on contraction. The pellet should be so admitted as to occupy the centre of the capillary when a steady temperature is attained. Rubber connections as shown in the dotted lines are made to apply equal pressures inside and

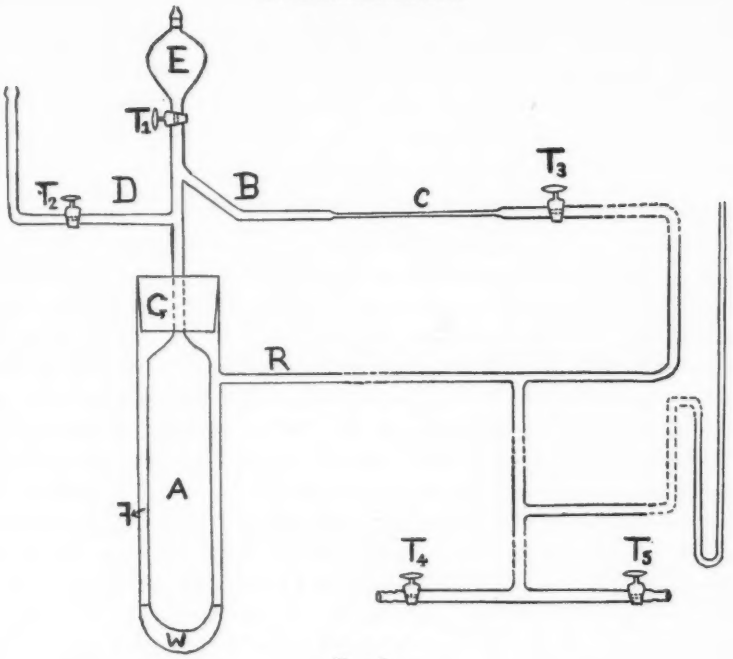


Fig. 1.

outside the inner vessel through the capillary C and the joint R respectively. The upper end of the outer jacket is closed with a one-holed rubber cork G that tightly fits in. The pressure that is applied by an ordinary foot-ball bladder pump by opening the stop-cock T_4 is measured by the manometer M and is released by the opening of the stop-cock T_5.

Constants and standardisation of the piezometer.—The volume of the piezometer is determined by exhausting the liquid that completely fills it into an empty graduated jar. Different liquids are taken and their mean volume is noted as the volume of the piezometer. In the present investigation the volume is 153 c.c.

As the volume of the piezometer is not much, a fine capillary is taken so as to get a shift of about 4 to 5 cm. for a pressure of one atmosphere. The capillary is calibrated twice with clean mercury and the mean volume for a shift of 1 cm. length has been found to be 0·003449 c.c.

In all the experiments pressures up to 60 cm. of mercury are first applied and the pressure is then suddenly released. There is not much capillary action here as all the glass connections are of sufficiently wide bore. The pressures are measured accurately up to 0·1 cm.

The shift of the mercury pellet is noted on the sudden release of the pressure in the apparatus. If this shift corresponds to a volume compression dv (the product of the length of the shift and the mean volume per cm.) the adiabatic compressibility β_ϕ is given by

$$\beta_\phi = \frac{dv}{\text{V.P.}}$$

V is the volume of the piezometer and P the pressure in atmospheres. A correction for the change in volume which the piezometer itself undergoes due to the compressibility of the glass of which it is made is to be introduced in the above. The cubical compressibility of soft glass according to Amagat (1889) is 0·0000022. As the volume of the liquid compressed is the same as the volume of the glass, the correction to be applied is the compressibility of the glass itself. Thus we have

$$\beta_\phi = \frac{dv}{\text{V.P.}} + 0{\cdot}0000022.$$

Before measuring the compressibilities of the oils, two standard liquids are taken and their adiabatic compressibilities are noted at the temperatures given. For comparison, the values of Tyrer are given alongside in Table II. In the course of the experiments it is observed that the values are reliable only if the pellet of the mercury is pure and dry before it is introduced* and no liquid adheres to the capillary on the side of the mercury pellet where pressure is applied.

TABLE II.

Adiabatic Compressibility of Two Standard Liquids.

Liquid	Temperature in °C.	Adiabatic compressibility $\beta_\phi \times 10^6$ (Author)	$\beta_\phi \times 10^6$ (Tyrer)
Benzene ..	26·1	72·8	71
Carbon tetrachloride ..	26·7	79·8	77

The agreement is considered satisfactory and the method is now applied for the determination of the adiabatic compressibilities of the oils under investigation. The results which are obtained by taking the mean of a dozen observations in each case are given in Table VI.

* Otherwise the pellet breaks within the capillary on releasing the pressure.

Specific volume and dv/dt.—In the present investigation a special type of pyknometer shown in Fig. 2 is used for determining the specific volume and its variation with temperature.

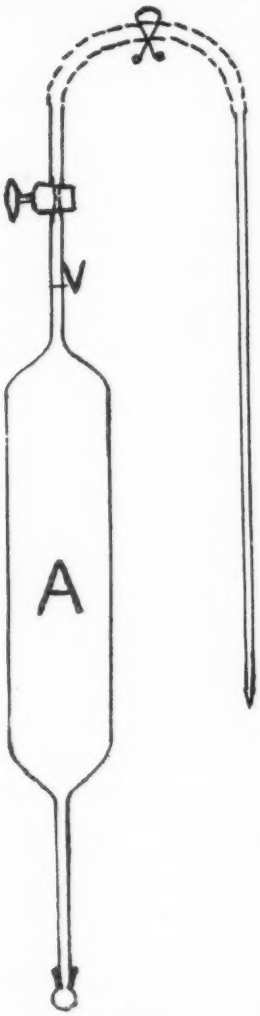


FIG. 2.

A is the cylindrical portion of the pyknometer ending in capillary tubes with a ground joint at the bottom and a stop-cock at the top. A mark *V* is made on the stem so that liquids may be sucked up to the mark. The fine adjustment of the liquid level is made by means of a tapered capillary tube attached with a pinch-cock to the upper end of the pyknometer. The volume of the pyknometer at the room temperature is first determined in the following manner. Double distilled water is taken in a test-tube at the room temperature and is sucked up to the mark. Closing the stop-cock *T*, the pyknometer is taken out, inverted, and the ground joint cap is put on the end. Knowing the weight of the water, and its density, its volume is calculated and found to be 27·8675 c.c. at 27·4°C. Assuming the cubic expansion of soft glass as 9×10^{-6} the volume of the pyknometer at any other temperature is easily obtained. To verify this, the density of water itself is determined at three different temperatures and the results are found to agree quite satisfactorily with the values given in *I.C.T.* (see Table III). The determination of the density is made in the following manner. The pyknometer is immersed in a pyrex test-tube just sufficient to hold the required quantity of the liquid. The test-tube with its contents is placed in an electrically heated water-bath the temperature of which is controlled to 0·1°C. by adjusting the current in the circuit. The object of heating the pyknometer also is to see that it acquires the same temperature as the liquid itself.

TABLE III.

Density of Water at Different Temperatures.

Temperature °C.	Density observed	Density from *I.C.T.*
46·7	0·98978	0·98953
70·0	0·97783	0·97781
81·7	0·97117	0·97072

The densities and therefrom the specific volumes of all the oils are determined at seven temperatures ranging from 25°--85°C. The specific volume at any temperature may be represented by a general equation of the type

$$v_t = v_0 + at + \beta t^2$$

where v_0, a and β are constants. These constants are determined by taking three values of v_t of the oil at three different temperatures. From this equation dv/dt can be calculated at any temperature. The following tables give the densities and specific volumes of the oils at the temperatures noted. The variation of the specific volume with temperature in each case is represented by the equation given under the corresponding table.

TABLE IV.

Densities and Specific Volumes of the Oils.

(*a*) *Eucalyptus oil.*

Temperature in °C.	Density	Specific volume
25·3	0·91894	1·0882
38·1	0·90864	1·1105
47·9	0·89976	1·1114
57·95	0·89200	1·1212
68·4	0·88291	1·1326
78·0	0·87437	1·1437
85·0	0·86863	1·1512

$v_t = 1·065050 + 0·00087357\ t + 0·0_516472\ t^2$

(*b*) *Cajeputi oil.*

Temperature in °C.	Density	Specific volume
27·4	0·90537	1·1045
37·6	0·89647	1·1155
47·8	0·88699	1·1274
58·4	0·88014	1·1362
68·8	0·87157	1·1474
76·4	0·86435	1·1569
84·9	0·85585	1·1684

$$v_t = 1 \cdot 082699 + 0 \cdot 00069095\, t + 0 \cdot 0_5 38209\, t^2$$

(*c*) *Coriandri oil.*

Temperature in °C.	Density	Specific volume
26·5	0·86276	1·1591
35·7	0·85517	1·1694
45·4	0·84710	1·1805
55·7	0·83830	1·1929
64·4	0·83023	1·2045
76·5	0·82020	1·2182
85·0	0·81242	1·2309

$$v_t = 1 \cdot 13194 + 0 \cdot 00096164\, t + 0 \cdot 0_5 23828\, t^2$$

(*d*) *Anisi oil.*

Temperature in °C.	Density	Specific volume
27·9	0·97794	1·0217
39·2	0·96824	1·0328
49·0	0·95983	1·0418
58·8	0·95165	1·0508
67·9	0·94508	1·0581
77·1	0·93723	1·0670
84·4	0·93132	1·0738

$$v_t = 0{\cdot}99411 + 0{\cdot}901011\,t - 0{\cdot}0_6 80101\,t^2$$

(*e*) *Citronellæ oil.*

Temperature in °C.	Density	Specific volume
26·9	0·84125	1·1887
38·0	0·83393	1·1991
48·3	0·82619	1·2104
58·2	0·82060	1·2186
67·1	0·81347	1·2293
75·4	0·80768	1·2381
85·2	0·80112	1·2483

$$v_t = 1{\cdot}16684 + 0{\cdot}00074672\,t + 0{\cdot}0_5 24507\,t^2$$

(*f*) *Santali oil.*

Temperature in °C.	Density	Specific volume
27·4	0·94700	1·0560
39·4	0·94012	1·0637
49·6	0·92843	1·0771
58·0	0·92622	1·07965
68·0	0·91734	1·0901
76·6	0·91175	1·0968

$$v_t = 1 \cdot 03964 + 0 \cdot 000513956\, t + 0 \cdot 0_{5}303186\, t^2$$

(*g*) *Cocoanut oil* (*Unscented*).

Temperature in °C.	Density	Specific volume
27·6	0·91784	1·0895
38·5	0·91074	1·0980
47·4	0·90279	1·1077
59·9	0·89575	1·1164
66·8	0·89078	1·1226
78·8	0·88240	1·1333
84·5	0·87897	1·1377

$$v_t = 1 \cdot 06747 + 0 \cdot 000782006\, t + 0 \cdot 0_{6}58060\, t^2$$

(*h*) *Cocoanut oil* (*Scented yellow lily*).

Temperature in °C.	Density	Specific volume
28·2	0·91708	1·0904
37·7	0·91127	1·0974
47·5	0·90365	1·1066
55·0	0·89857	1·1129
70·0	0·88598	1·1287
81·0	0·88095	1·1351

$v_t = 1 \cdot 06714 + 0 \cdot 000817026\, t + 0 \cdot 0_6 27072\, t^2$

(*i*) *Groundnut oil.*

Temperature in °C.	Density	Specific volume
27·7	0·90764	1·10176
39·3	0·90120	1·10962
48·6	0·89506	1·11724
59·1	0·88880	1·12510
68·2	0·88218	1·13355
78·0	0·87530	1·14246
84·8	0·87097	1·14816

$v_t = 1 \cdot 08557 + 0 \cdot 00050945\, t + 0 \cdot 0_5 26963\, t^2$

(*j*) *Castor oil.*

Temperature in °C.	Density	Specific volume
27·5	0·95450	1·04767
50·0	0·93832	1·06567
73·8	0·92464	1·08150

$v_t = 1 \cdot 025269 + 0 \cdot 000822578\, t - 0 \cdot 0_6 291325\, t^2$

Specific heat at constant pressure.—An electrical method is followed for the determination of the specific heats of oils. Nearly 8·5 cm. of fine nichrome wire is taken as the heating coil and is soldered to copper leads. Its resistance is carefully determined with a standard post-office box to be 1·154 ohms. A calibrated ammeter with a least count of 0·05 amperes is included in series with the heating coil. A current of the order of 2 amperes from an accumulator of 4 volts is passed through the coil till the temperature rise is about 5°C. Radiation correction is applied and the specific heat is calculated in the usual manner. For purposes of check, the specific heats of benzene, carbon disulphide and carbon tetrachloride have been determined by this method as 0·423, 0·246 and 0·206 at 31°·4C. and 30°·0C. and 31°·9C. respectively. These compare very satisfactorily with the figures taken from *I.C.T.*, namely, 0·420, 0·243 and 0·201. The specific heats thus determined for the various oils are noted in Table V.

TABLE V.

Specific Heats of Oils at Constant Pressure.

Oil	Temperature in °C.	Specific heat at constant pressure
Eucalyptus oil	32·7	0·420
Cajeputi oil	31·9	0·429
Coriandri oil	32·5	0·536
Anisi oil	32·4	0·411
Citronellæ oil	32·4	0·485
Santali oil	32·7	0·509
Cocoanut oil (unscented) ..	32·1	0·461
Cocoanut oil (scented) ..	32·4	0·462
Groundnut oil	32·0	0·433
Castor oil	32·5	0·489

Isothermal compressibility.—The physical properties measured above permit us to calculate the isothermal compressibility with the help of the

well-known thermodynamical relation

$$\beta_T = \beta\phi + \frac{T\left(\frac{dv}{dt}\right)^2 \times 1{\cdot}013 \times 10^6}{J \times v \times C_p}$$

dv/dt, J, v and C_p represent respectively the rate of variation of specific volume with temperature, mechanical equivalent of heat, specific volume and the specific heat at constant pressure. The values of β_T so calculated are given in Table VI. The value of γ which is the ratio of β_T to $\beta\phi$ is incidentally noted and it is found that it varies from 1·11 to 1·32 in the oils studied.

TABLE VI.

Adiabatic and Isothermal Compressibilities of Oils.

Name of the oil	Temperature in °C.	$\beta\phi \times 10^6$	v	$\frac{dv}{dt}$	C_p	$\beta_T \times 10^6$	$\gamma = \frac{\beta_T}{\beta\phi}$
Eucalyptus oil ..	28	74·04	1·090753	·00096565	0·420	88·85	1·20
Cajeputi oil ..	26·7	68·8	1·102096	·00087970	0·429	83·61	1·22
Coriandri oil ..	26·7	71·73	1·159315	·00108888	0·536	85·57	1·19
Anisi oil	26·1	51·23	1·009960	·00096938	0·411	67·62	1·32
Citronella oil ..	25·1	69·37	1·187127	·00086974	0·485	78·85	1·14
Santali oil ..	25·3	52·95	1·054586	·00066727	0·509	58·95	1·11
Cocoanut oil (unscented) ..	26·5	60·91	1·088601	·00081278	0·461	70·45	1·16
Cocoanut oil (scented) ..	26·5	60·48	1·088981	·00083142	0·462	70·37	1·16
Groundnut oil ..	29·5	59·25	1·102945	·00066853	0·433	66·12	1·12
Castor oil ..	29·8	47·47	1·049524	·00080522	0·489	56·73	1·20

4. *Refractive Index, Rotation of the Plane of Polarisation and Depolarisation Factor.*

The refractive indices for the D line of all the oils are determined at the temperatures noted against their valus with an Abbe-Refractometer.

Most of the oils rotate the plane of polarisation the value of which varies according to the specimen. To have an idea of the rotation of the plane of polarisation, the rotation for the D line is measured with a Lippich triple shade Polarimeter. It will be noticed from Table VII that the rotation of

the plane of polarisation is either absent or very small in all the oils studied except santali and coriandri. We may, therefore, infer that the values of the depolarisation factors are not much affected on this account. Even in the latter two cases, it may easily be shown that the error arising out of this rotation of plane of polarisation will be negligibly small as a very small cubical cell (2 cm. side) has been used for making these measurements.

The depolarisation factor of the scattered light is measured using the well-known Cornu method. A carbon arc is used as the source and a good quality Zeiss lens of 8 cm. focal length employed to condense the light into the cubical cell (2 cm. side). The depolarisation factor is determined both with full light and with light filtered through a thick red glass interposed between the lens and the cell. The latter procedure is calculated to eliminate fluorescence. The values for cocoanut oil, groundnut oil and castor oil are taken from Jogarao's work (1936) .

TABLE VII.

Refractive Index, Rotation of the Plane of Polarisation and Depolarisation Factor of Oils.

Name of the oil	Temperature in °C.	Refractive index D line	Opt. rotation produced by a column of 10 cm. at 29°C. D line	$\rho_u \times 100$ full light	$\rho_u \times 100$ red light
Eucalyptus oil ..	26·0	1·4548	+ 0°·17	57·8	36·0
Cajeputi oil	26·5	1·4623	− 1°·99	41·4	32·3
Coriandri oil	25·5	1·4639	+ 8°·81	58·4	34·7
Anisi oil	25·3	1·5530	Nil	68·7	75·8
Citronellæ oil ..	28·5	1·4667	− 1°·51	46·9	34·7
Santali oil	28·5	1·5041	+25°·46	47·8	33·8
Cocoanut oil (unscented)	28·5	1·4532	Nil	69·9	42·2
Cocoanut oil (scented) ..	29·0	1·4533	Nil	..	..
Groundnut oil	28·5	1·4668	Nil	62·5	35·5
Castor oil .. .	29·1	1·4760	+ 4°·01	57·5	46·0

5. Intensity of the Scattered Light and Comparison with Theory.

The use of the rotating sector for the visual measurement of the intensities of the scattered radiation is advisable only in the case of liquids where there is no fluorescence. Most of the oils investigated here exhibit fluorescence and with a view to eliminate errors arising on this score, a photographic method is used in the present work. Light from a quartz mercury point source lamp running on a current of 2·25 amperes is focussed with a good Zeiss lens of 8 cm. focal length into the cubical cell containing the liquid. The scattered radiation is focussed by another lens on to the slit of a constant deviation spectrograph. The slit is kept sufficiently wide so as to record an image enveloping the wing, if any. During the work, the positions of the point light, the lens, and the cell, are kept fixed. The current through the lamp is kept constant by drawing it from a battery. The oils are divided into two groups one of the weaker and other of stronger intensities. Spectra scattered by each set of oils are exposed on a separate plate along with that scattered by pure and dust-free benzene for comparison. In the first group an exposure of two hours for each one of the oils is found to be necessary and in the second, an exposure of one hour for each one of the oils is found to be sufficient. Separate intensity marks for each set are furnished by the method of varying slit widths and the intensities of the λ 4358 group of lines in the oils are compared with that of benzene in the usual manner. The density-log intensity curves are obtained with the help of a Moll recording microphotometer. The values so obtained are given in Table VIII on the scale benzene = 3·2, ether = 1.

The following expression gives the intensity of the light scattered by a liquid :

$$\frac{I_{liq}}{I_2} = \frac{\pi^2}{2\lambda^4 r^2} \cdot \frac{R_T \beta_T}{N} \cdot (n^2 - 1)^2 \frac{6 + 6\rho_{liq.}}{6 - 7\rho_{liq.}}$$

The various letters have their usual significance. Under identical conditions of I_0, r, λ and T, the intensity of the scattered radiation of any one liquid can be compared with that of another in the following manner :

$$\frac{I_1}{I_2} = \frac{\beta_{T_1} (n_1^2 - 1)^2 (6 + 6\rho_1)}{\beta_{T_2} (n_2^2 - 1)^2 (6 + 6\rho_2)} \frac{(6 - 7\rho_2)}{(6 - 7\rho_1)}$$

If benzene is chosen as the second liquid, knowing its physical constants, the ratio I_1/I_2 may be calculated from the above expression for each one of the oils studied in the present paper. The values so calculated on the scale benzene = 3·2, ether = 1 are given in Table VIII for comparison with the experimentally determined values.

TABLE VIII.

Intensity of Light Scattering in Oils.

Name of the oil	Nature of fluorescence	Intensity observed (Benzene=3·2)	Intensity calculated (Benzene=3·2)	Intensity observed (Jogarao)
Eucalyptus oil ..	Nil	1·38	1·82	..
Cajeputi oil ..	Nil	1·38	1·69	.
Coriandri oil ..	Nil	1·66	1·76	..
Anisi oil ..	Nil	13·8	14·4	..
Citronellæ oil ..	Faint	3·2	1·64	..
Santali oil ..	Faint	1·5	1·45	..
Cocoanut oil ..	Strong	(9·6) ?	1·71	2·4
Groundnut oil ..	Weak	2·02	1·43	2·24
Castor oil ..	Moderate	(3·2) ?	1·74	1·92

The experimental results show a good agreement with the calculated values in practically all cases except the more viscous vegetable oils. The intensity in these cases is obviously largely spurious as no special precautions have been taken to remove the suspended dust particles. Moreover, the fluorescence in these cases is also more marked. In fact, earlier results obtained in this laboratory by Jogarao (1936) and quoted in column 5 of Table VIII bring out this feature prominently. These results have been obtained by Jogarao using red light for illumination and working with samples of vegetable oils which have been rendered completely dust free by elaborate centrifuging and hence show better agreement with the calculated values. In the results obtained by the author, the very high value which is predicted by the theory for anisi oil and confirmed satisfactorily by the experiment is noteworthy.

Thus the results of the present investigation strongly support the statement that the intensity of the scattered light is of molecular origin in the essential oils as well as in the Indian vegetable oils studied.

6. Raman Spectra and Constitution of the Oils.

In this section the results of a study of the Raman spectra of five of the above essential oils are given. Light from a six-inch quartz mercury arc

has been condensed on to a Wood's tube filled with the pure oil. The Raman spectra are photographed on golden-isozenith plates using a Hilger two-prism glass spectrograph. In all cases, filters consisting of either quinine sulphate or sodium nitrite solutions have been used in the path of the incident light. The exciting radiation is thus confined to the group of lines λ 4358 only and the continuous spectrum due to fluorescence is also considerably reduced. The results which are given below in Tables IX to XIII are followed by a brief discussion in relation to the chemical constitution of the oils. Photographs of the Raman spectra are reproduced in the plate.

TABLE IX.

Raman Frequencies in Eucalyptus Oil.

Intensity	$\Delta\nu$ (Author)	$\Delta\nu$ (Cineole) Bonino & Cella	Intensity	$\Delta\nu$ (Author)	$\Delta\nu$ (Cineole) Bonino & Cella
5*b*	2973	2971	0	985	..
5*b*	2922	2925	6*b*	926	933
2*b*	2877	..	1	891	..
3	1487	1486	1	865	870
5*b*	1455	1452	1	843	..
5*b*	1434	1409	5	813	825
0	1358	1363	1	762	..
0	1315	..	10	653	665
5	1272	1280	0	..	603
2	1240	1230	6	546	558
3	1214	..	3	508	518
5	1167	1166	4*b*	446	461
2	1109	1121	2	387	391
3	1079	1098	4	302	305
2	1053	1033	1	262	253
5	1017	..	0	215	220

TABLE X.

Raman Frequencies of Cajeputi Oil.

Intensity	$\Delta\nu$	Intensity	$\Delta\nu$
3*b*	2964	0	957
3*b*	2924	3	925
1*b*	2878	0	882
1*b*	1648	0	842
5*b*	1456	1	812
5*b*	1436	0	763
0	1372	?	725
0	1311	10	651
2	1277	?	613
0	1237	?	580
0	1206	3	546
2*b*	1163	1	502
1	1108	3*b*	446
1	1079	0	384
0	1050	1	306
2	1015	0	258
0	981	..	..

TABLE XI.

Raman Frequencies of Coriandri Oil.

Intensity	$\Delta\nu$ (Author)	Strong lines of Linalol (Bonino & Cella)	Intensity	$\Delta\nu$ (Author)	Strong lines of Linalol (Bonino & Cella)
0	3005	..	2*b*	1446	..
0	3944	..	2	1384	..
1	2917	2923	1	1300	1292
0	2870	..	0*b*	920	928
2	1675	1672	0	812	..
1	1641	..	0	760	..

TABLE XII.

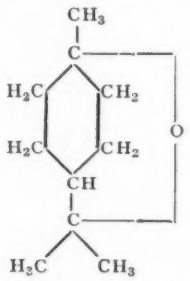
Raman Frequencies of Anisi Oil.

Intensity	$\Delta\nu$	Intensity	$\Delta\nu$
1*b*	3122	3	1284
1*b*	3050	1	1245
10	1656	1	1212
10	1608	3	1176
0	1557	0	1072
0	1509	0	848
0	1450	0	820
0	1413	0	793
0	1373	1	757
3	1307	1	644

TABLE XIII. *Raman Frequencies in Citronellæ Oil.*

Intensity	$\Delta\nu$ (Author)	Strong lines in Geranial and Citronellal (Bonino & Cella)	Intensity	$\Delta\nu$ (Author)	Strong lines in Geranial and Citronellal (Bonino & Cella)
3*b*	2953	2959	4*b*	1451	1452
5*b*	2911	..	3	1384	1385
5*b*	2873	2881	1	1309	..
10	1633	..	?	1238	..
10	1597	..	..	..	..

The frequencies given by the author for eucalyptus oil are the mean values of three sets of measurements. With the exception of a few lines, the results of Bonino and Cella obtained with cineole agree very satisfactorily with those obtained by the author for eucalyptus oil. This confirms the view that cineole is the chief constituent of eucalyptus oil. Some of the weak lines that have been recorded by the author have been presumably missed by Bonino and Cella. Amongst the more prominent discrepancies may be noted the frequency at 1017 (5). The double line recorded in the present investigation at 1455 and 1434 has been measured by Bonino and Cella as a single line at 1452. It will be noticed from the table that a frequency 603 has been given by Bonino and Cella whereas it is not to be found in the author's results. It must be mentioned here that a line has been recorded in the required position but the author is of the opinion that this line is to be regarded as the same frequency as 653 but arising from λ 4347. It may further be noted that the carbon-hydrogen frequencies obtained in the region of 2900 and in the region of 1450 are typical of a saturated compound and this is in agreement with the structure of cineole shown below.



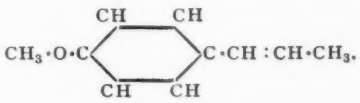
$C_{10}H_{18}O$ Cineole

The absence of any frequency in the region 1600 and 1700 corresponding either to a $c = c$ or $c = 0$ may be noted. The wings accompanying the Rayleigh lines are not at all marked. All these factors are in agreement with the accepted constitution of cineole.

It is very interesting to note that the Raman spectrum of cajeputi oil (Table X) is practically identical with that obtained in eucalyptus oil. The only difference that may be noted is the presence of a broad band at 1648 in the cajeputi oil in place of a line at 1487 in eucalyptus oil. Such a close similarity between the two spectra points to the well-known fact that cineole is the chief constituent of both cajeputi and eucalyptus oils. This similarity may also be seen in respect of all other physical properties investigated in the present paper.

The Raman frequencies obtained in coriandri oil are given in Table XI. The chief constituent of this oil appears to be dextro linalol (Allen). This compound in a pure state has been studied by Bonino and Cella and the strong frequencies obtained by them are also shown in Table XI for comparison. They occur in coriandri as well and we may therefore conclude that linalol forms a good portion of it. The presence of other lines however shows that there are other constituents also.

In Table XII the Raman frequencies obtained in anisi oil are given. The chief constituent of this oil is anethole (Allen). In certain samples, about 85 per cent. of the oil is said to be pure anethole. The chemical constitution of anethole is represented below.



$C_{10}H_{12}O$. β-Propenylphenylmethyl ether.

This compound in the pure state has been studied by Hayashi (1934) but the full results are not available to the author and hence a comparison could not be made. Amongst the notable features in the Raman spectrum of this compound, mention may be made of a strong pair of frequencies at 1608 and 1656. These are presumably characteristic of unsaturated carbon-carbon linkages in and outside the benzene ring. The presence of unsaturation and of a benzene ring in the structure are further borne out by the high depolarisation value and the large intensity of scattered light (see Tables VII and VIII) exhibited by this oil. There is also an appreciable wing accompanying the Rayleigh lines in this case.

The Raman frequencies obtained in oil citronellæ are given in Table XIII. The chief constituent of this oil is geranial and in some cases citronellal and citrol are also present, Bonino and Cella have studied citronellal and geranial in the pure state. Some of the strong lines namely 2959, 2881, 1452 and 1385 obtained by them, in these compounds are alao present in oil citronellæ.

7. *Summary.*

The adiabatic compressibility, rate of variation of specific volume with temperature, specific heat at constant pressure, rotation of plane of polarisation, refractive index, depolarisation factor and the intensity of scattered light have been measured for eucalyptus, cajeputi, coriandri, anisi, citronellæ, santali, cocoanut, groundnut and castor oils. From these data the isothermal compressibility and the ratio of specific heats are calculated for each oil with the help of thermodynamical equations. A piezometer similar to that described by Tyrer has been used for the compressibility measurements. A modified type of pyknometer has been used for the measurement of specific volumes. A spectrographic method is employed for the measurement of the intensity of the scattered light. For determining the other physical constants, usual methods have been adopted.

A comparison is made of the observed intensity of light-scattering with that calculated on the basis of the above physical constants. Good agreement is noted in most cases thus furnishing a support for the theory of light scattering.

Raman spectra of five of the essential oils, namely, eucalyptus, cajeputi, coriandri, anisi and citronellæ, have been photographed using a two-prism glass spectrograph. The results are discussed in relation to the known chemical constitution of the chief constituents of the various oils.

In conclusion, the author desires to express his grateful thanks to Mr. S. Bhagavantam, Head of the Department of Physics, for his kind interest and constant guidance throughout the progress of this work. He is also thankful to Dr. A. Veerabhadra Rao for his helpful suggestions.

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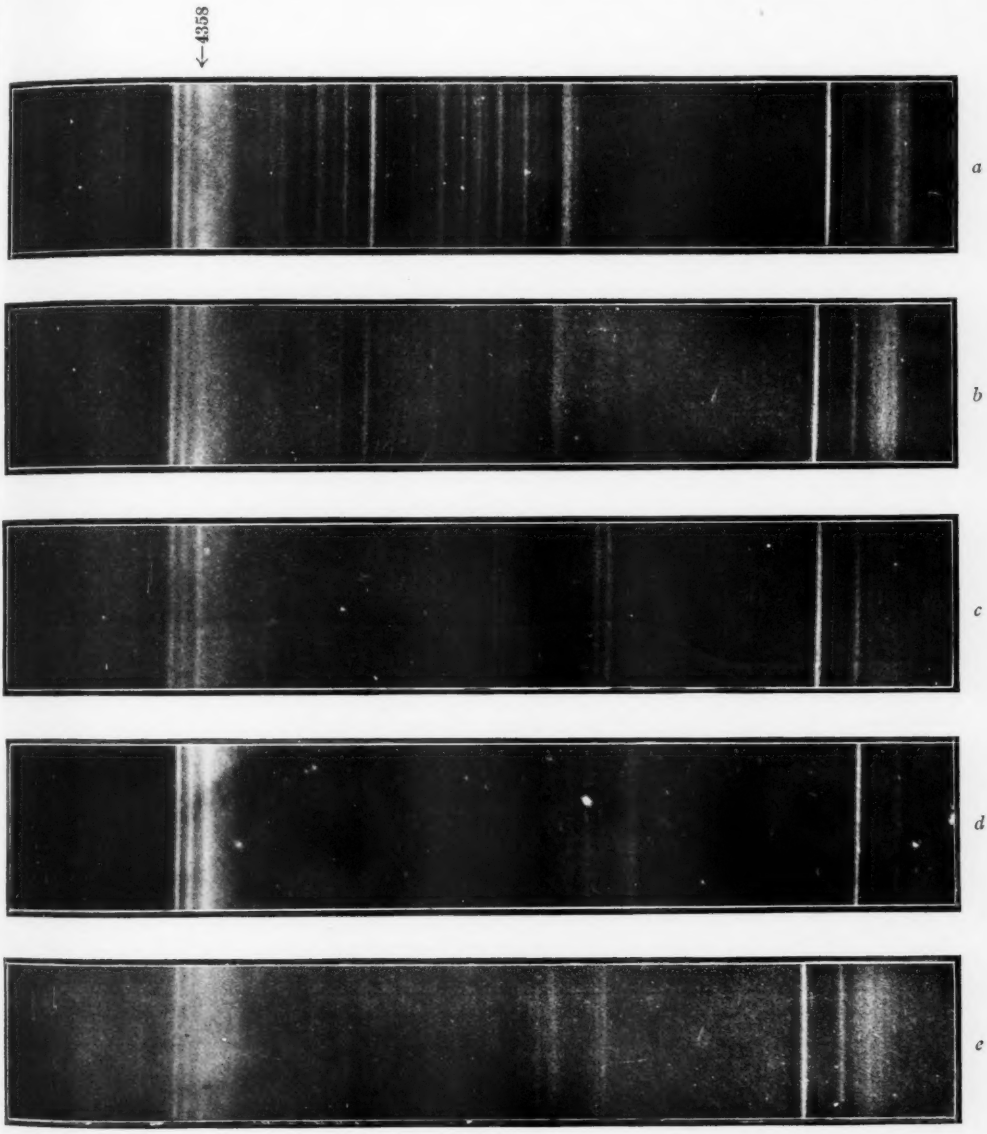

Raman Spectra.

a. Eucalyptus oil; *b*. Cajeputi oil; *c*. Anisi oil; *d*. Citronellæ oil; *e*. Coriandri oil.

DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part III. Platinum, Copper, Selenium and Tellurium Sols.

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1. Introduction.

In Parts I and II of this series (Krishnan, 1937), the author has reported the measurements of the depolarisation factors of six gold sols and six silver sols for different wave-lengths from 2500 to 7000 A.U. It has been found that in these sols in the region of the specific absorption, the depolarisation factors show an enormous increase. From a comparison of the observed depolarisation and absorption curves with the theoretical ones it has been inferred that the particles in gold and silver sols behave optically like elongated ellipsoids with the axial ratio equal to 0·75. The investigations have been extended to sols of other elements. In this paper the results obtained from a study of the absorption and the scattering of light in platinum, copper, selenium and tellurium sols are given.

Gans and Calatroni (1920) measured the absorption coefficient of some protected platinum sols prepared according to Bredig's method and also Paal's method using hydrazine hydrate as reducing agent. Comparing the observed values of the absorption coefficients with the values calculated from Mie's theory they concluded that the colloidal particles of platnium are approximately spherical in shape. Very recently Gribnau (1936) has calculated the absorption coefficient and the scattering power of selenium sols on the basis of Mie's theory of the colour of metallic turbid media. Up till now no quantitative measurements have been made either of the absorption coefficient, the dispersion of refractive index or the dispersion of depolarisation of light-scattering in platinum, copper, selenium and tellurium sols.

2. Preparation of the Sols.

Platinum sol I was prepared according to the method suggested by Lottermoser (1901). To 25 c.c. of a solution containing 0·6 g. of chloroplatinic acid per litre were added 4 c.c. of a 0·2 N sodium hydroxide solution. The mixture was heated to boiling. After the flame was removed, 5 c.c. of formaldehyde solution containing 1 c.c. of formaldehyde in 100 c.c. of water were added. The mixture was again heated, and while it was boiling briskly, 5 c.c. more of the dilute formaldehyde solution were added. A dark brown sol resulted at once. The sol was diluted to 125 c.c. by adding pure double-distilled water. A very small quantity of sodium citrate was added to increase the stability of the sol.

Platinum sol II was prepared according to Bredig's method. This is one of the most important methods for preparing relatively pure sols of platinum. An arc was struck between two platinum electrodes immersed in freshly distilled double-distilled water contained in a resistance glass beaker. The beaker was kept at 0°C. by surrounding it with freezing mixture. A direct current of 5-6 amperes was passed at 220 volts for about a few seconds. A very dilute dark brown sol resulted at once. This sol was allowed to stand for a couple of days. After the heavy particles, if any, had settled down, the clear sol was decanted into a hard glass bottle.

Copper sol.—As compared with silver or platinum sols copper sols are, in general, more difficult to prepare and less stable in the absence of protecting agents. Accordingly most copper sols are protected. Relatively stable olive-green to brown-green hydrosols are readily prepared by passing an arc between copper wires under water according to Bredig's method. This method was employed for the preparation of the copper sol. The sol was coloured brown.

Selenium sol I.—Probably the most satisfactory method of preparing stable unprotected sols of selenium consists in the reduction of a solution of selenium dioxide with hydrazine hydrate. To obtain sols of quite uniform particle size, the method suggested by Kruyt and Van Arkel (1923) was employed. 90 c.c. of water and 5 c.c. of 1·5 M hydrazine hydrate were heated to 100°C. and 4 c.c. of 0·1 M selenium dioxide were added. After the mixture had become dark yellow, 1 c.c. more of the selenium dioxide solution was added. The heat was then removed, and after the mixture had stood for ten minutes it was diluted to 400 c.c. with pure water. In this procedure the particles formed by the original reduction serve as nuclei and grow on the addition of a second portion of selenium dioxide without

the formation of new particles. The sol was entirely clear by transmitted light. The sol was diluted four times before it was used for measurements.

Selenium sol II was prepared in the following manner: 90 c.c. of water and 4 c.c. of 0·1 M selenium dioxide were heated to 100°C. While the mixture was boiling 5 c.c. of hydrazine hydrate were added to the mixture. After the solution had turned yellowish red the heat was removed and the mixture was allowed to cool and after ten minutes it was diluted to 400 c.c. with pure double-distilled water. This sol contained particles the size of which was smaller than that of particles in sol I.

Since the selenium sols were rather sensitive to the action of light, the sols had to be stored in the dark. The observations were made with these sols as quickly as possible.

Tellurium sol.—The colloid chemistry of tellurium parallels that of selenium in most respects except that stable tellurium sols are more difficult to prepare in the absence of protecting agents. Although a number of reducing agents have been employed in the preparation of tellurium sols, hydrazine hydrate is by far the most important in forming both unprotected and protected sols. In the present case the tellurium sol was prepared according to the method suggested by Doolan (1925). 0·5 g. of telluric acid was dissolved in 50 c.c. of boiling water, adding the hydrazine hydrate drop by drop until turbidity almost occurs. The sol which resulted was diluted to a total volume of 250 c.c. The bluish opalescent sol formed in the hot contained aggregates which were peptized by further addition of water, giving a quite stable sol.

3. *Absorption and Depolarisation Measurements.*

The method employed for the measurements of the extinction coefficients and the depolarisation factors ρ_u, ρ_v and ρ_h from λ 2500 to λ 7000 A.U. is exactly similar to the one employed in the case of silver sols (see Part II). It was found that in the case of platinum and copper sols no appreciable change in the values of ρ_u, ρ_v and ρ_h was observed even on diluting the sols to 50 per cent. It follows from this that in the case of these sols the particular concentration used in each case had no influence on the depolarisation factors. In the case of selenium and tellurium sols such a test could not be made since the particles were peptized on further dilution.

A correction arising from the finite angle of convergence of the incident beam was applied to the observed values of ρ_u and ρ_v, the correction for

ρ_h being neglible. The values of ρ_u, ρ_v and ρ_h for the six sols are given in Tables II and IV. The extinction coefficients are given in Tables I and III.

Curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissæ. They are reproduced in Figs. 1 and 3. The values of ρ_u are plotted against wave-length. The curves are reproduced in Figs. 2 and 4.

TABLE I.

Extinction Coefficients.

Wave-length in A. U.	Platinum Sol I	Platinum Sol II	Copper Sol
2250	$>1\cdot8$	0·55	0·8
2500	$>1\cdot8$	0·53	0·8
2750	$>1\cdot8$	0·5	0·79
3000	$>1\cdot8$	0·45	0·775
3250	$>1\cdot8$	0·4	0·75
3500	1·4	0·35	0·66
3750	1·0	0·31	0·51
4000	0·7	0·28	0·37
4250	0·6	0·265	0·30
4500	0·525	0·25	0·25
5000	0·4	0·23	0·19
5500	0·335	0·21	0·15
6000	0·28	0·19	0·11
6500	0·24	0·17	0·07
7000	0·22	0·15	0·05

TABLE II.

Dispersion of Depolarisation.

Wave-length in A. U.	Platinum Sol I			Platinum Sol II			Copper Sol		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	4·9	1·00	31	12·0	..	..	2·1	..	..
3650	4·2	1·00	32	12·15	0·5	2·8	2·0	0·57	39·5
4046	4·2	1·00	33	12·5	0·5	3·2	1·85	0·53	40
4358	4·0	1·00	35	12·55	0·5	3·8	1·7	0·5	41
4750	3·9	1·00	38	10·55	0·46	4·8	1·2	0·46	62
5000	3·8	0·93	40	8·7	0·44	5·3	1·0	0·42	72
5500	3·8	0·93	40	8·1	0·38	5·8	0·77	0·32	71
6000	3·4	..	..	7·6	0·32	6·2	1·5	0·7	88
6500	3·0	..	..	7·1	0·30	6·7	1·76	..	..

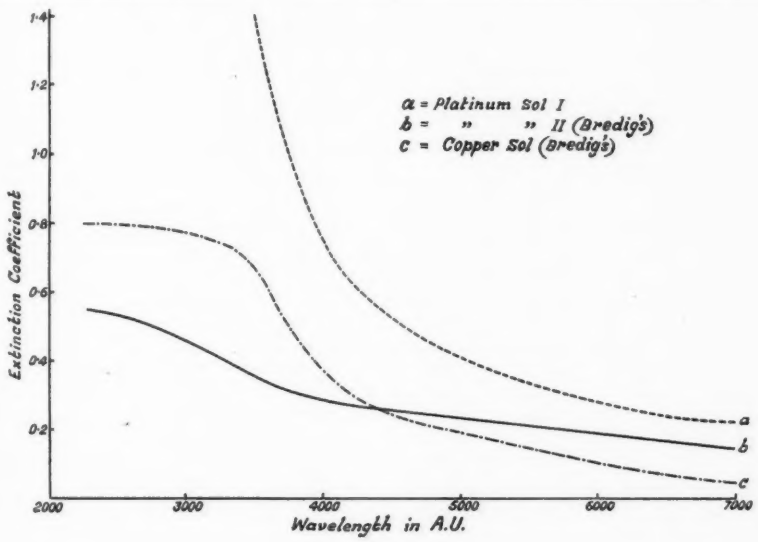

FIG. 1.

Extinction Coefficients.

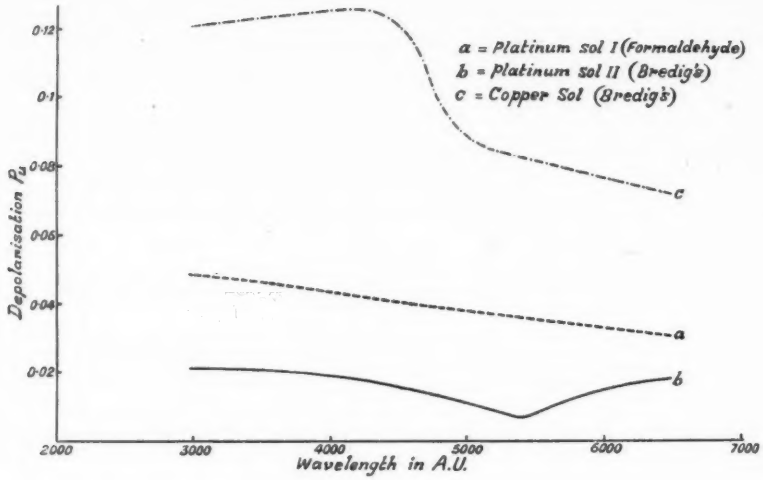

FIG. 2.

Dispersion of depolarisation factor ρ_u.

TABLE III.

Extinction Coefficients.

Wave-length in A.U.	Selenium Sol I	Selenium Sol II	Tellurium Sol
2250	1·2	0·9	1·8
2500	1·21	0·8	1·78
2750	1·23	0·67	1·68
3000	1·26	0·57	1·5
3250	1·3	0·48	1·16
3500	1·35	0·4	0·93
3750	1·39	0·34	0·72
4000	1·44	0·3	0·59
4250	1·48	0·27	0·5
4500	1·47	0·25	0·43
5000	1·3	0·2	0·33
5500	0·88	0·17	0·25
6000	0·47	0·13	0·2
6500	0·275	0·11	0·16
7000	0·19	0·07	0·125

TABLE IV.

Dispersion of Depolarisation.

Wavelength in A.U.	Selenium Sol I			Selenium Sol II			Tellurium Sol		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2536	..	..	..	91	..	..	..	..	..
2967	−71·4	0·9	0·6	84	0·27	0·33	96·5	4·0*	4·2
3650	78·3	0·8	1·0	70	0·22	0·38	50·8	2·85*	5·8
4046	43·8	0·7	1·5	27	0·16	0·49	27·1	2·2*	8·8
4358	34·7	0·65	1·75	23	0·15	0·62	24·8	2·3*	9·9
4750	23·8	0·6	2·5	12·5	0·15	0·8	19·8	1·97	10·8
5000	21·8	0·6	3·1	10·3	0·12	1·5	15·6	1·7	12·0
5500	13·2	0·47	5·1	7·2	0·12	2·2	8·8	1·2	15·5
6000	8·2	0·37	6·2	6·0	0·12	3·0	8·0	1·2	18·9
6500	3·8	0·25	13·0	4·9	0·12	4·6	6·4	0·8	22·0

* Indicates that these values of ρ_v are calculated from the observed values of ρ_u and ρ_h.

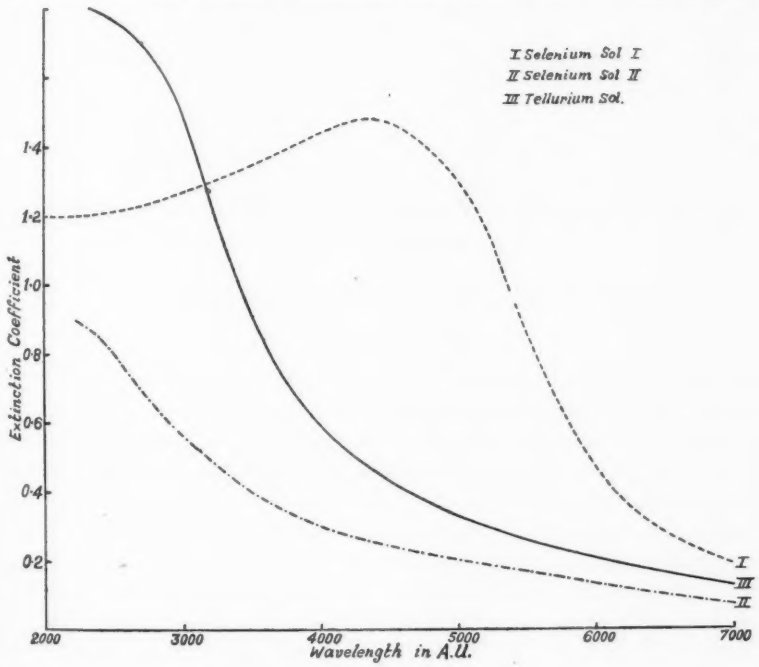

FIG. 3.

Extinction Coefficients.

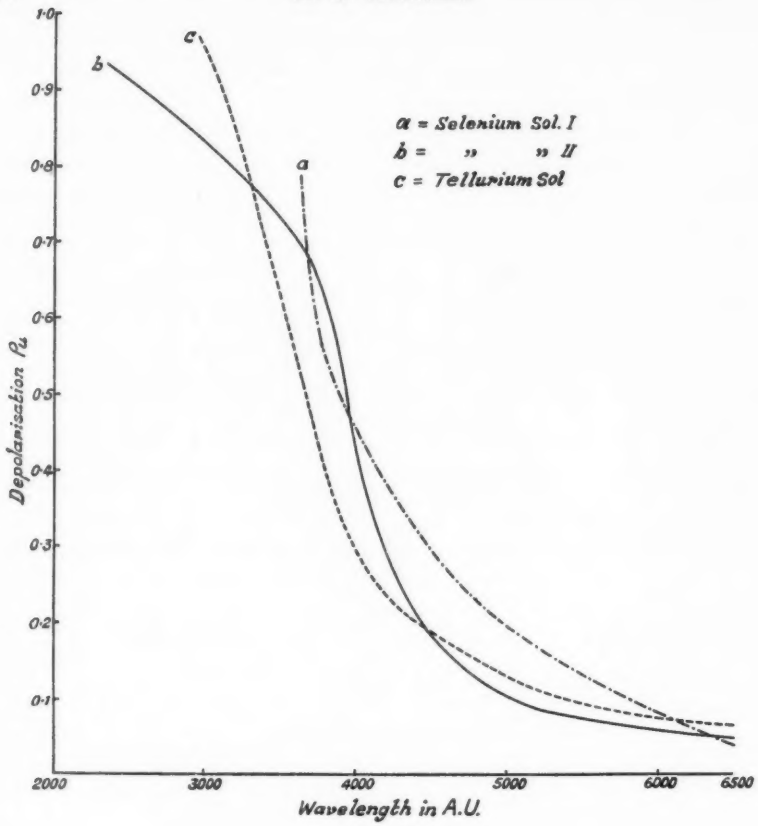

FIG. 4.
Dispersion of depolarisation factor ρ_u.

4. Discussion of Results.

Unlike gold and silver sols, the sols of platinum, copper, selenium and tellurium do not possess any specific absorption in the visible and in the ultra-violet regions. The extinction coefficient goes on increasing continuously as we proceed towards the ultra-violet region. However, the curve of absorption for selenium sol I shows a maximum at about 4500 A.U. In the case of sols which possess regions of characteristic absorption, the depolarisation factors ρ_u, ρ_v and ρ_h all increase with diminution in wave-length, whereas in the case of platinum, copper, selenium and tellurium sols ρ_u and ρ_v increase with diminution in wave-length and ρ_h decreases. This kind of dispersion is characteristic of the finite size of the particles. With diminution in wave-length the apparent size of the scattering particles increases,

i.e., a/λ, (a = diameter of the particle and λ = the wave-length), increases. Consequently the depolarisation factor ρ_u should evince an increase and the factor ρ_h should show a corresponding decrease. This is what has been observed in these sols. Slight increase in the value of ρ_v indicates that as one proceeds towards the ultra-violet region the optical anisotropy of the particles does increase to some extent.

Platinum sol.—For both the sols of platinum the value of ρ_h is definitely less than 100 % showing thereby that the particles in these sols are of size comparable with the wave-length of light. The extremely low value of ρ_v indicates that these particles are almost spherical in shape. Comparing the values of ρ_u, ρ_v and ρ_h for the two sols it is seen that the particles in the Bredig's sol are much larger in size and more symmetrical in shape than the particles in the other sol (see Tables I and II and Figs. 1 and 2).

TABLE V.

Absorption Coefficients of Platinum sol.

Wave-length λ in A.U.	Rod	Sphere	Disc
4250	0·0638	0·0202	0·116
4500	0·0614	0·0188	0·113
5000	0·0624	0·0144	0·117
5500	0·0649	0·0114	0·124
6000	0·0669	0·0087	0·129
6500	0·0725	0·0067	0·14

Table V gives the absorption coefficients of a platinum sol calculated according to Gans' theory (Gans, 1912, 1920). For particles in the form of rods and discs, the absorption coefficient is greater in the red region than in the violet region, whereas for spherical particles the variation is in the opposite direction. The latter corresponds to the experimentally observed data. Comparing the theoretical values with the experimental values, one finds that the particles in the two sols of platinum should be more like spheres.

Copper sol.—Just as the platinum sol, copper sol also gives comparatively small depolarisation values. The observed depolarisation ρ_u shows

a minimum at 5500 A.U. (see Table II and Fig. 2). But the quantity $\rho_u - \frac{2\rho_v}{1+\rho_v}$ does not show any such minimum. It goes on diminishing from a value of 0·8 per cent. at 3650 to a value of 0·1 per cent. at about 6000 A.U. This quantity corresponds to the depolarisation due to the finite size of the scattering particles. Although the size of the particles is larger than the molecular dimensions, it is not of the order of the wave-length of light. From the comparatively low value of ρ_v one is led to believe that the particles are approximately spherical in shape. Table VI gives the values of the absorption coefficient and the depolarisation ρ_u for very small particles of ellipsoidal shape, calculated according to Gans' theory. The values of the reflective power and the extinction coefficients for metallic copper are taken from

TABLE VI.

Extinction Coefficients and Depolarisation Factor of Copper Sol calculated according to Gans' Theory.

Wave-length λ in A. U.	Rod		Sphere	Disc	
	k	ρ_u %	k	k	ρ_u %
3480	43·0	70	67·6	39·1	46·8
3950	43·4	62·6	69·6	48·2	39·6
4500	33·6	80·6	61·6	35·6	36·1
5000	28·7	67·3	51·0	33·4	35
5500	24·7	93·3	59·8	23·8	37·8
6300	12·0	84·7	18·7	17·2	31·9

the paper of Maxwell Garnett (1906). The absorption curves for a sphere and a disc show a maximum at about 5500 A.U., whereas that for a rod progressively diminishes with the wave-length. The experimental curve also does not show any maximum in this region. From this it can be concluded that if the shape of the particles deviates from sphericity, the deviation should be in the direction of a prolate spheroid.

Selenium and tellurium sols.—The curves of absorption and depolarisation for selenium and tellurium sols are somewhat similar. The dispersion of ρ_u in both the cases is something remarkable. It has a value of 4 per

cent. at about 6500 A.U., whereas it assumes the value of 100 per cent. in the far ultra-violet. Such an increase in the value of ρ_u is characteristic of selenium and tellurium sols (see Table IV and Fig. 4). Both ρ_v and ρ_h are very small and in the ultra-violet region they become almost equal. In selenium sol I, it is found that ρ_h is $< \rho_v$ for 2967. These sols contain particles of approximately spherical in shape. It is well known that the particles in sulphur suspensions are also spherical in shape. As would be expected, the colloid chemistry of selenium is similar to that of sulphur and to that of tellurium. The stability of the sol decreases as we go from sulphur to selenium and from selenium to tellurium. Another striking difference that comes out from a comparative study of the properties of these three sols is that the particle size is quite uniform in selenium and tellurium sols, whereas sulphur sol usually contains particles of varying sizes. Unlike tellurium and sulphur sols, selenium sols are very easily affected by light. The rate of increase of ρ_u for selenium sols and tellurium sols is much greater in the violet region than in any other region of the spectrum. The optical properties of metallic selenium and tellurium do not show any striking dependence on wave-length. The depolarisation factors indicate that the degree of dispersion is greater in selenium sol II than in sol I. As in the case of colloidal sulphur, there is only one maximum in the light absorption curve for selenium sols, and this moves towards smaller and smaller wave-length with increasing degree of dispersion of the sol. Comparing the experimental curve of absorption for selenium sol I with the theoretical curves (Gribnau, 1936) calculated according to Mie's theory, it is seen that the size of the particles in this sol should be of the order of 150 $\mu\mu$.

The sols of platinum, copper, selenium and tellurium should not be expected to show any appreciable magnetic or flow birefringence, since the particles in these sols are spherical in shape. The experiments of Diesselhorst and Freundlich (1916) and Bjornstahl (1924) on the flow and magnetic birefringence in platinum sols go to show that the particles are of spherical shape. In the case of other sols experimental data are wanting.

The author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his keen interest in the work.

5. *Summary.*

Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h and the extinction coefficient of platinum, copper, selenium and tellurium sols are made for different wave-lengths from 2500 to 7000 A.U. These sols do not possess any region of specific absorption. The depolarisation factors ρ_u and ρ_v are

found to increase and ρ_h is found to decrease as we proceed towards the ultra-violet. The rate of increase of ρ_v in the case of selenium and tellurium sols is very much greater than in the case of the platinum and copper sols. The extremely low values of ρ_v and ρ_h indicate that the particles in these sols are spherical in shape. The finite value of ρ_u, however, is indicative of the appreciable size of the scattering particles in these sols.

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X-RAY ANALYSIS OF THE STRUCTURE OF A FIBROUS MODIFICATION OF TOURMALINE.

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and
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1. *Introduction.*

The well known mineral tourmaline is a complex silicate occurring as well-defined crystals belonging to the rhombohedral hemimorphic class and is pleochroic. The ferruginous variety containing titanium, *viz.* schorl, like most silicates, is macroscopically black with a pitchy lustre. A few samples of iron tourmalines presented to one of us by the Director of the Mysore State Geological Department were found to exhibit a distinctly fibrous structure. These specimens were thought particularly interesting since tourmaline, unlike amphiboles and serpentines, is not usually described as occurring as a fibrous modification. Apart from a remark by Weinschenk and Clark[1] and some isolated instances of the occurrence of fibrous tourmaline[2] there does not seem to be any literature on this modification of tourmaline.

The crystal structure of tourmaline has not yet been completely worked out although Machatschki[3] has been able to suggest a formula for the mineral from a consideration of his own X-ray investigations and the chemical analyses of various workers. He suggests that the probable formula is $XY_9Si_6Be_3H_xO_{31}$ where X and Y are cations of one kind or another. The mineral belongs to one of the hexagonal space groups C_{3v}^1 or C_{3v}^2 and has three molecules in the unit cell. The unit cell dimensions vary about the values $a = 16{\cdot}23$ and $c = 7{\cdot}26$ Å.[4]

The present work was undertaken in order to find out if any essential difference existed between the structures of ordinary tourmaline and its fibrous modification. Work on similar lines carried out on fibrous modifications of amphiboles and serpentines (commonly known as asbestos) by

[1] Weinschenk and Clark, *Petrographic Methods*, 1932, p. 235.
[2] *Handbuch der Mineralogie*, Band II, pp. 347 and 354.
[3] Machatschki, *Zs. Krist.*, 1929, **24**, 924.
[4] R. W. G. Wyckoff, *The Structure of Crystals*, 1931, p. 326.

G. L. Clark[5] and his collaborators has been helpful in understanding their formation.

2. *Description of Specimens.*

The specimens of tourmaline used in this investigation bore the index numbers O_{1564} and Q_{16} in the records of the Geological Department of Mysore.

O_{1564} is reputed to have come from the Bababudan area in the Mysore State. The exact locality, however, is not known. This specimen is compact and massive at the core and distinctly fibrous at the margin. The core is jet black with a resinous lustre. There is a gradation towards a distinct fibrous condition at the margin. The fibres are grey, sharp and brittle and possess a silky lustre. In the extremely modified state they are distinctly asbestiform, ash grey in colour and very friable falling easily to powder. The individual fibres are very brittle and inelastic.

The specimen Q_{16} was found in a quartz vein in the granite gneiss exposed in the channel section near Mardipur Saddle in the Maddur branch of the Irwin canal. The specimen is a crystalline aggregate of quartz and tourmaline intimately intergrown. The tourmaline is black and has a shining metallic lustre. It is brittle and has prominent striations. Single crystals of Q_{16} of suitable dimensions were used for purposes of taking comparison photographs since no such crystals with well defined faces were obtainable from specimens of O_{1564}.

3. *Experimental.*

The mineral specimens were cut into small pieces, about two or three millimetres long by about quarter of a millimetre thick. In the case of Q_{16} small single crystals of suitable size were available and were employed. Specimens from the fibrous portions were so cut that their lengths were along the direction of the fibres. The completely modified portion could be divided into specimens of the required type without much effort since it was easily friable. Specimens from the central core were also cut so that their lengths were parallel to the direction in which the fibres were running in their marginal portions. These specimens were mounted in the camera with their lengths perpendicular to the X-ray beam.

For taking the photographs a continuously evacuated X-ray tube supplied by "Seemann Laboratorium" was used with a copper anode. It was supplied with a constant tube potential of about 40 k.v., the tube current being about 10 m.a. Under these conditions good photographs

[5] G. L. Clark and Anderson, *Ind. Eng. Chem.*, 1929, **24**, 924.

could be obtained in about an hour or an hour and a half. A flat camera was used in which the specimen to film distance was 47·63 mm., this distance being obtained in the usual way from sodium chloride powder photographs.

The single crystal specimens of Q_{16} were mounted with their c axes perpendicular to the X-ray beam and rotated during exposure. The fibrous specimens were oriented with their fibre axes perpendicular to the X-ray beam and were not rotated. Specimens from the central core of the mineral were also not rotated during the exposure. The fibrous specimens gave typical fibre patterns one of which is reproduced in Fig. 1. The central core gave a pattern consisting of isolated spots superposed on a very faint fibre pattern. From this it was at once evident that the central core was essentially a single crystal while the fibrous portion was an aggregate of fibrously oriented small crystals. In order to find out whether the crystallographic character of the modified part was different from the core powder photographs of both of them were obtained.

4. *Results.*

The pattern given by the core of the mineral consists of a number of isolated spots, similar to what should be expected from a sligthly distorted single crystal, superposed on a very faint fibre pattern. The fibre pattern consists of arcs of circles which subtend an angle of about 10° at the central spot.

The ash grey fibrous part of the mineral having a distinct silky lustre gives the pattern reproduced in Fig. 1. This is a typical fibre pattern and very closely resembles the single crystal rotation pattern of Q_{16} given in Fig. 2. Also this fibre pattern is the same as the faint fibre pattern in the photographs of the central core. The corresponding spots of the two fibre patterns coincide if the two photographs are superposed on one another.

From the resemblance of the fibre pattern of Fig. 1, with the single crystal rotation pattern of Q_{16} about the c axis (Fig. 2) it follows that the fibre axis in the former case is the c axis. The identity period along the fibre axis calculated from measurements of the fibre pattern of Fig. 1 is 6·98 Å. The length of the c axis of the unit cell obtained from the rotation photograph of Q_{16} is 7·08 Å. These are of the same order and thus provide further evidence to show that the fibre axis of the modified part of the mineral is the c axis. The a axes are randomly oriented. The structure of the outermost fibrous part which easily crumbles to powder is also similar since its patterns are identical with the fibre pattern of Fig. 1.

Powder patterns of the core and the fibrous modification were identical there being no measurable difference in the diameters of the various rings in the two patterns. From measurements of both powder and fibre patterns the dimensions of the unit cell arrived at are given below :—

$$Q_{16}, \quad a = 15{\cdot}94 \text{ Å}, \quad c = 7{\cdot}08 \text{ Å}$$
$$O_{1564}, \quad a = 15{\cdot}94 \text{ Å}, \quad c = 6{\cdot}98 \text{ Å}$$

From a consideration of the above results one can conclude that both the core and the outer fibrous part of the mineral are probably one and the same material, *viz.* tourmaline. Their powder patterns are identical showing that the dimensions of their unit cells are also the same. But the core is essentially a single crystal or a mosaic of crystallites oriented with all their axes parallel or nearly so, in which the fibrous modification is also present in small quantities here and there. The marginal portions are almost completely fibrous consisting of crystallites of tourmaline oriented fibrously with the *c* axis as the fibre axis. The *a* axes of these crystallites are oriented at random.

It is with much pleasure that we take this opportunity to express our sincere thanks to Sir C. V. Raman, F.R.S., for his kind interest in the progress of this investigation. Our thanks are also due to Mr. B. Rama Rao, Director of Geology in Mysore State, for the gift of the tourmaline specimens used in this work.

Summary.

The structure of a fibrous modification of tourmaline has been investigated by methods of X-ray diffraction. The fibrous modification is found to have essentially the same unit cell dimensions as the unmodified core of the mineral. In the fibrous modification the tourmaline crystallites are found to be oriented fibrously, the *c* axis being the fibre axis. The *a* axes are oriented at random.

Note added in proof :—While this paper was in preparation a note has been published by one of us in *Current Science*,[6] on the chemical analysis of the fibrous tourmaline used for this investigation.

[6] K. Y. Srinivasa Iyengar, *Current Science*, 1937, **5**, 535.

FIG. 1.

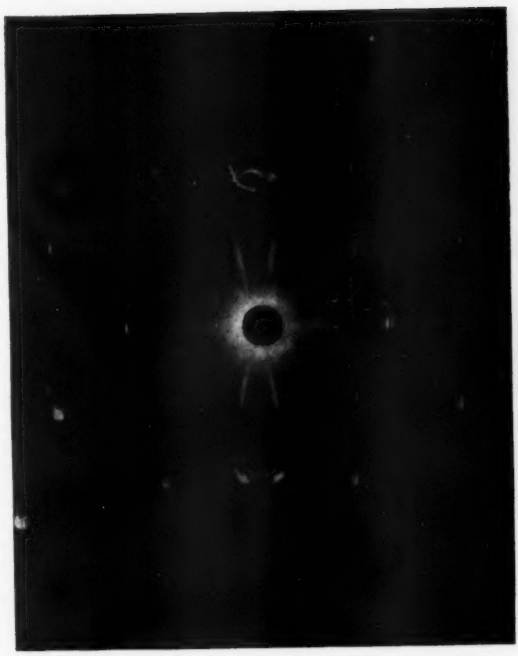

FIG. 2.

NOTE ON THE ABSORPTION SPECTRUM OF PHOSPHOROUS PENTASELENIDE VAPOUR.

By Mohd. Israrul Haq and R. Samuel.
(From the Department of Physics, Muslim University, Aligarh.)

Received February 12, 1937.

The absorption spectra of pentoxides and pentasulphides of elements of group V, such as N_2O_5, P_2O_5 and P_2S_5* have been investigated in the vapour state.[1,2,3] The beginnings of the various regions of selective absorption indicate an energy difference equal to the excitation of the ^1D and ^1S term of O and S respectively. It has been concluded, that the photo-dissociation processes follow a formula such as

$$1/2\ P_2O_5 + h\nu = 1/2\ P_2O_3 + O,$$

the oxygen or sulphur atom being in various low states of excitation. Thermochemical calculations which are possible, *e.g.*, for N_2O_5, support this view.[3]

Such an interpretation can be tested again by the absorption spectrum of P_2Se_5. The bond energies being weaker, the whole spectrum should be shifted towards longer waves. But the energy difference of the long wave limits of the two first absorption regions should agree with the term difference $^1D - {}^2P$ of Se which is 1·18 e.v.

We have investigated the absorption spectrum of P_2Se_5 with the same apparatus, described earlier[4] in an absorption cell of length 80 cm., one maximum of selective absorption and the beginning of a second one have been obtained. No bands due to Se_2 could be seen. On the photometer record the wave-length of the maximum was determined at λ 2780. The two long wave limits lie at $\lambda\lambda$ 3420 and 2534. Their energy difference is therefore 1·3 e.v. in good agreement with the excitation energy of Se (^1D). Compared with N_2O_5, P_2O_5, and probably also with P_2S_5 the first long wave limit is shifted

* The first absorption region with a beginning at λ 4900 of P_2S_5, to our mind, is extremely doubtful. The density of the spectrum produced by the H_2 continuum here approached rapidly the threshold value of the plate. Compounds of such very slight yellow colouring, as a rule, exhibit a long wave limit in the ultraviolet (for the vibrationless molecule). Furthermore, also the absorption of S_2 lies in this region. The energy difference of the following limits (1.5 e.v.) corresponds to that of $^1D - {}^3P$ of S (1.1 e.v.) inside the experimental error, since the first beginning of a continuous absorption spectrum is never well defined. We consider λ 3180 as the true beginning of the spectrum.

towards longer waves. We therefore believe that the two regions of selective absorption correspond to the dissociation processes $1/2\ P_2Se_5 \rightarrow 1/2\ P_2Se_3 + Se\ (^3P)$ and $1/2\ P_2Se_5 \rightarrow 1/2\ P_2Se_3 + Se(^1D)$.

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ABSORPTION SPECTRA OF SOLUTIONS OF SOME HALIDES AND OXYHALIDES OF S, Se AND Te.

By R. Samuel and M. Usman.

(From the Department of Physics, Muslim University, Aligarh.)

Received February 11, 1937.

Recently Hussain and Samuel[1] have investigated the absorption spectra of vapours of halides and oxyhalides of Se and Te with a view to correlate the various regions of selective absorption to particular photodissociation processes. They used comparatively low temperatures, mostly between 100° and 250° C. and their results are in close agreement with those obtained for the corresponding more stable compounds of sulphur.[2] Furthermore as far as the molecules $TeCl_2$ and $TeBr_2$ are concerned they are in agreement with certain observations of Larionov,[3] who measured the discrete band spectrum of these substances and gives also some preliminary figures on the continuous absorption. But these substances easily decompose and some are rather unstable as can be seen from the experiments of Damiens,[4] who concludes, that, *e.g.*, $TeCl_2$ and $TeBr_2$ exist in the vapour phase only whereas in the crystalline state they form solid solutions $Te + TeX_4$. It appeared therefore to be advisible to measure the absorption spectrum of these substances when dissolved in neutral solvents because here it should be possible to avoid decomposition. It was, however, not possible to find suitable solvents for all of them. Spectra of $SOBr_2$ dissolved in hexane, of $SeOCl_2$, $SeBr_4$, $TeBr_2$ and TeI_2 in ether and of Se_2Br_2 in carbon tetrachloride have been measured. For all other substances a neutral solvent could not be found. $SeCl_4$ dissolved in glacial acetic acid has been measured, but here the possibility of complex formation and chemical reactions is already great. Moreover, on account of the self-absorption of these solvents, it has not been possible to reach wave-lengths smaller than about λ 2400.

The absorption spectra were examined by the quantitative method described by one of us earlier,[5] simplified by the use of a stable and continuous source of light giving rise to the continuous hydrogen spectrum. The absorption coefficient K is defined by the equation $I = I_0 \cdot 10^{-kcd}$ in which I_0 and I represent the intensity of light before and after absorption, c and d stand for the concentration and thickness of the solution respectively. The results are shown in Figs. 1 to 6 and in Table I. For $SeOCl_2$, where

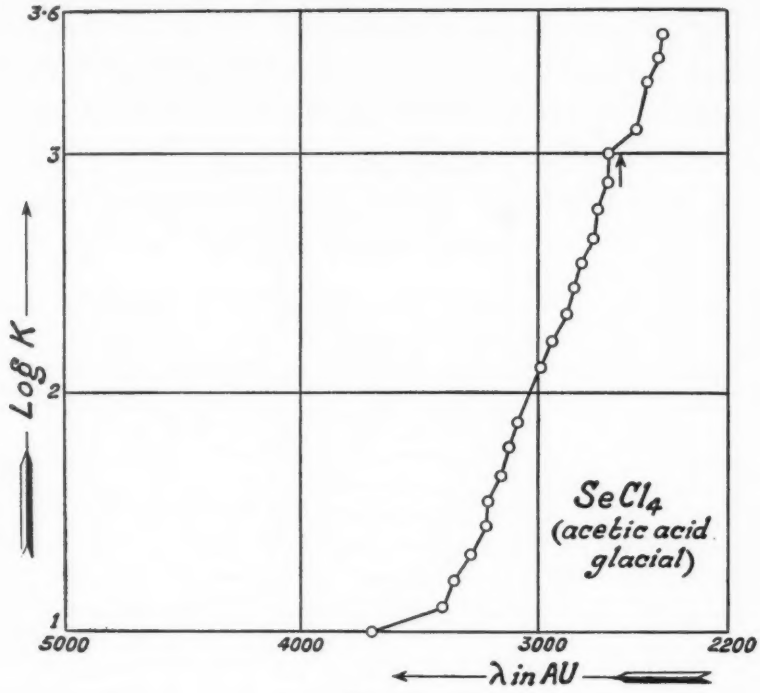

FIG. 1.

the maximum of absorption could not be reached on account of self-absorption of the solvent, a spectrum ($c = 0{\cdot}02$, $d = 0{\cdot}05$) has been examined along with the corresponding one through ether alone by means of the recording microphotometer and the wave-length has been taken from the photometer record.

In the diagrams of Figs. 1 to 6, the value of log K is plotted against λ, as usual. This logarithmic representation produces a flattening of the absorption curve and if the difference in the K values of the various maxima is not big enough to become appreciable in the log K scale, the maxima appear as points of inflection only. In general any compound becomes less transparent for shorter waves and hence the maxima in this representation will be overlapped by a continuous ascent of the curve towards shorter waves. Wherever the absorption curve indicates a true deviation from a smooth course, we have therefore taken the point of inflection at the shorter wave as an indication of a superimposed maximum. Only in some cases of very broad regions of absorption the approximate middle of such a part of the

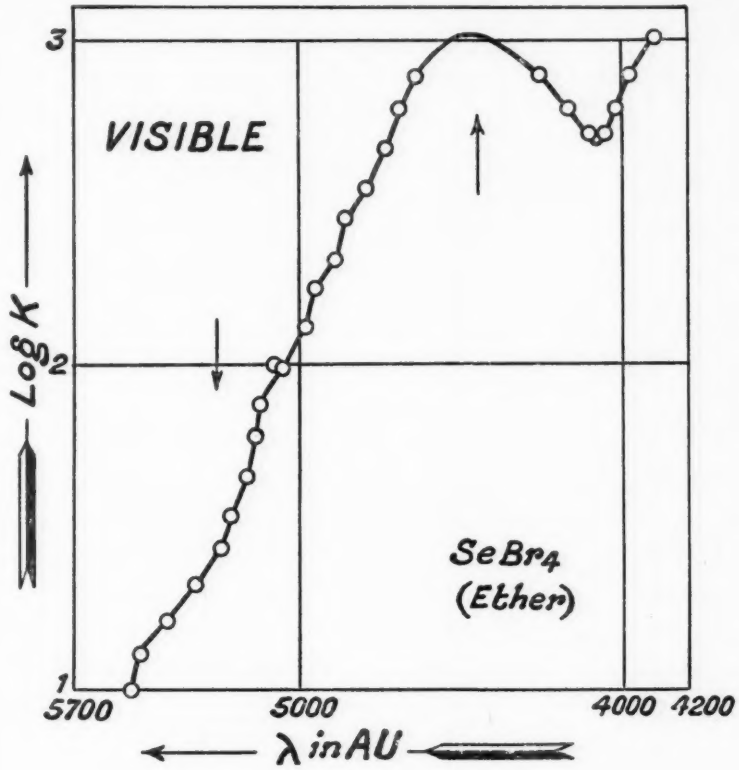

FIG. 2.

absorption curve has been taken into account. Throughout only such deviations from the smooth course have been considered, which are indicated by more than one, mostly by several successive points, going away from the smooth course of the log K curve. These points of inflection have been marked by arrows in the diagrams.

Table I shows, that in no case the maxima in solution lie exactly at the same frequency as in the vapour state. This has to be expected and is doubtless due to the various effects of solvation, discussed elsewhere.[6] But it can be seen, that the maxima found in the vapour state are also present in the solution spectrum, as far as it could be examined. All the maxima appear to be present and no new ones have been found. We take this as an indication, that the maxima found in the vapour state are due to the undecomposed compounds. Only in $SeCl_4$ the results differ for solution

TABLE I.

Maxima of Selective Absorption in

	I Max.	II Max.	III Max.	IV Max.
$SOBr_2$ Vapour	..	327	265	..
in hexane	..	303	257	
$SeCl_4$ Vapour	..	327	265	..
in glacial actetic acid ..	..	..	(275 ?)	..
$SeOCl_2$ Vapour	..	..	266	..
in ether	..	..	250·5	..
$SeBr_4$ Vapour	490	427	262	..
in ether	525	445	~ 315	..
Se_2Br_2 Vapour	..	384	322	257
in CCl_4	..	390	338	..
$TeBr_2$ Vapour	473	380	314	228
in ether	446	383	316	..
TeI_2 in ether	510	390	310	..

and vapour. The first maximum could not be obtained at all and the second one is doubtful. Since the compounds dissolved in neutral organic solvents show the same maxima as in the vapour state, we believe that the disagreement in the case of $SeCl_4$ is due to some reaction with the acetic acid.

It is well known that the beginnings of the various regions of selective absorption shift towards longer waves with increasing temperature, vapour pressure, or length of the absorbing layer. As discussed elsewhere[7] this is due to the increased number of molecules in excited vibrational levels

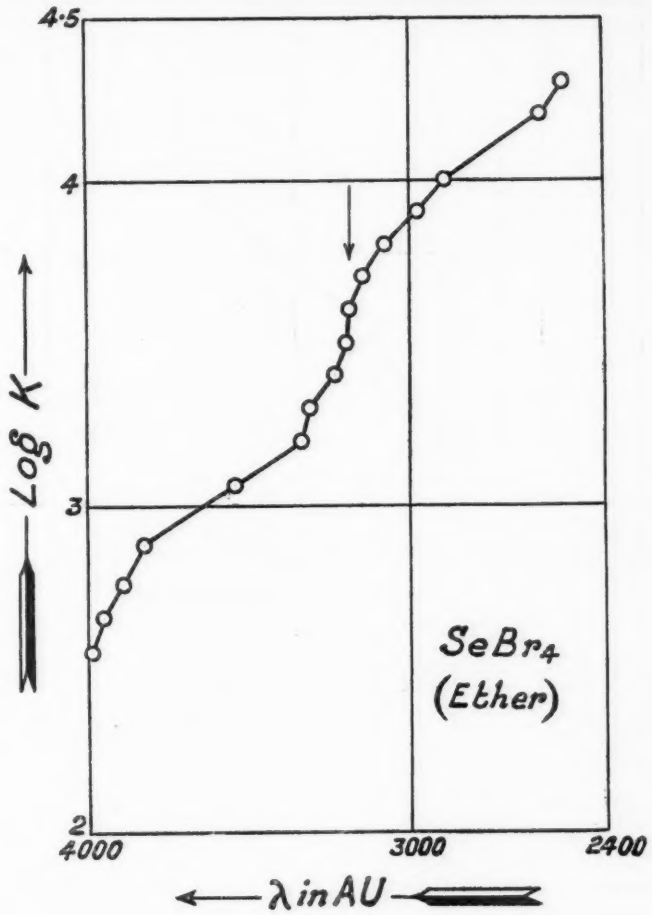

FIG. 3.

of the ground term. It is therefore of interest to compare the beginnings of selective absorption in solution with the red wave limits found in the vapour state. These points, which mark the beginning of a region of selective absorption are however still more difficult to determine in the log K scale. In some cases, however, they are very clearly indicated. Thus in the curve of Se_2Br_2 the beginning of absorption leading to the maximum at λ 338 lies doubtless at about λ 365, whereas in the vapour state λ 350 has been obtained. The first red wave limit, belonging to the maximum at λ ~ 390 is marked by another clear point of inflection at λ 450, while the corresponding value for

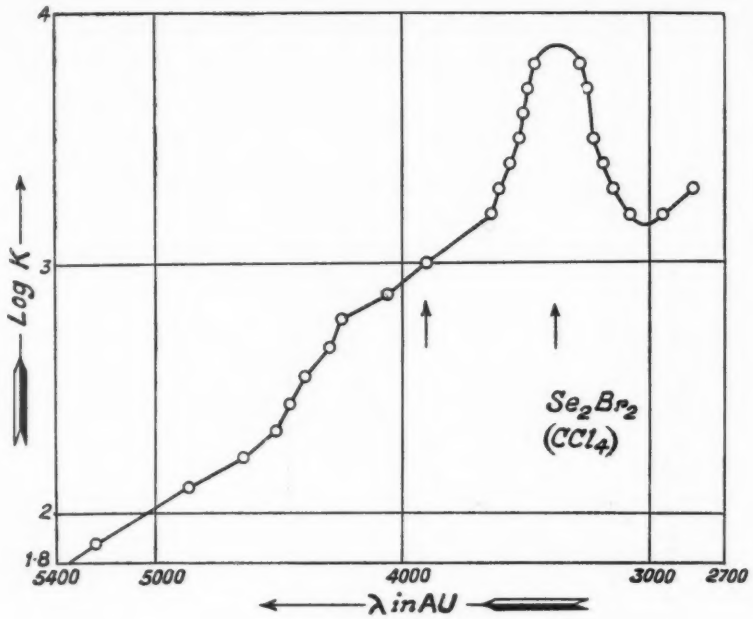

FIG. 4.

the vapour is λ 465. For $TeBr_2$ the beginning corresponding to the maximum at λ 383 doubtless lies at λ ~ 410, while in the vapour state λ 420 has been found. Again the beginning of the next region of selective absorption for which λ 340 has been found in the vapour state appears to be marked by an inflection of the curve at λ 335 in solution. The agreement is not quite so good for $SeBr_4$, but for $SOBr_2$ the photometer record of the absorption spectrum in solution indicates long wave limits at 365 and 269 $m\mu$ belonging to the maxima at λ 303 and 257 respectively, while the corresponding figures of these limits in the vapour state are 378 and 281 $m\mu$. This agreement supports the contention, discussed elsewhere[7], that the red wave limit in the vapour state will be identical with that of the vibrationless molecule, only, if the spectrum is taken at rather low vapour pressures. The shift towards longer waves is due to the molecules in excited vibrational levels. It can be seen, that the log K values of these red wave limits is generally only one unit or less lower than that of the corresponding maximum.

As the absorption spectra of these halides and oxyhalides do not essentially differ from those obtained in the vapour state, the corresponding photodissociation processes will be the same too, the energy values slightly modified

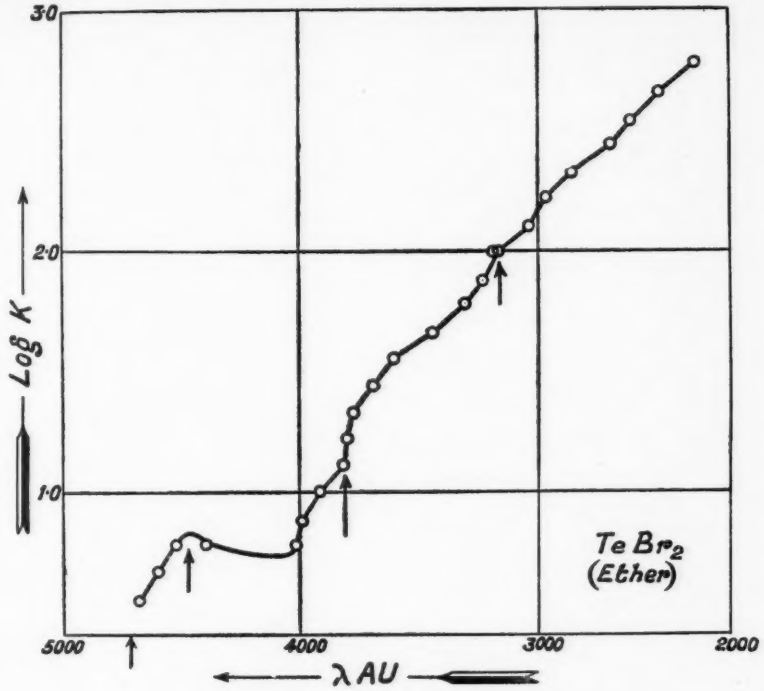
3·0
2·0
1·0
Log K
5000
4000
3000
2000
λ AU
Te Br2
(Ether)

FIG. 5.

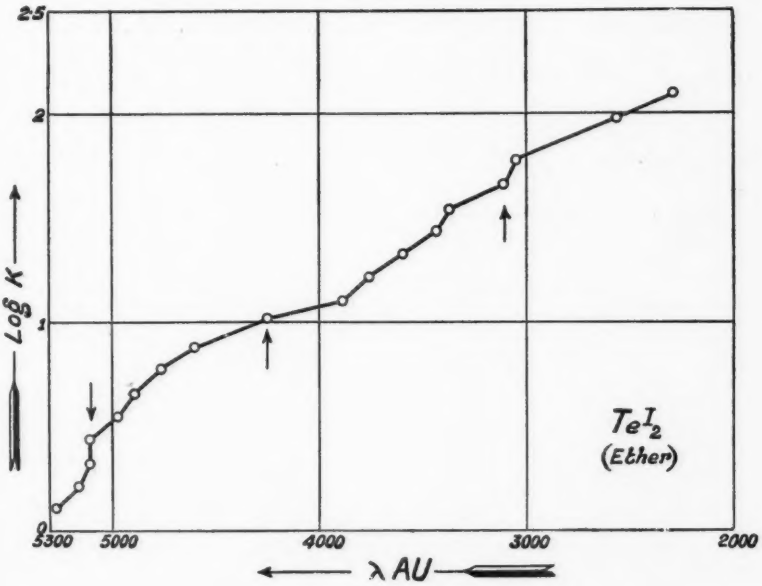
2·5
2
1
0
Log K
5300
5000
4000
3000
2000
λ AU
Te I2
(Ether)

FIG. 6.

on account of the energy of solvation. For the chlorides and bromides the correlation of the various maxima of selective absorption to certain bond energies have been discussed in detail for the vapour state[1] and need not be repeated here. For the Te – I bond in TeI_2 no thermochemical data are available. From the values 55 and 48 K. cal./mol. of the mean bond energy of the Te—Cl and the Te—Br bond respectively derived earlier[1], it appears as if the energy of the Te—I bond should lie near about 35 to 40 K. cal./mol. The TeI_2 spectrum shows three points of inflection which appear to mark three regions of selective absorption, with the wave-lengths λλ 510, 390 and 310. The first red wave limit cannot be determined from our measurements, but those belonging to the second and third one appear to be marked by inflection points at λλ 495 and 390, corresponding to 57 and 72 K. cal./mol. In analogy to $TeBr_2$ the third maximum should correspond to the simultaneous rupture of both the Te—I bonds, and the mean bond energy therefore would be 36 K. cal./mol. The second maximum should then denote a decomposition into TeI + I,* the iodine atom being in the excited $^2P_{\frac{1}{2}}$ state. The excitation energy of this term is 21·5 K. cal./mol. and the red wave limit at 57 K. cal./mol. agrees so well with $36 + 21{\cdot}5 = 57{\cdot}5$, that this correlation appears to be highly probable.

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ON THE LINEAR ALGEBRA OF CLASSES OF ELEMENTS IN A FINITE ABELIAN GROUP.

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Introduction.

Let $C_1, C_2, \ldots C_r$, be the complete conjugate classes of elements in a finite group G with the group operation say multiplication. If the product $C_i C_j$ denotes the totality of the elements obtained by multiplying each element of C_i by each element of C_j, it is known that each element of C_k occurs the same number of times γ_{ij}^k in $C_i C_j$. We then say that the classes C combine among themselves by multiplication, with the multiplication table:

$$C_i C_j = \Sigma \gamma_{ij}^k C_k.$$

Recently* Dr. R. Vaidyanathaswamy showed a more general kind of classification of elements in G defined by any group H of automorphisms of G. If an element S of G and all elements which correspond to S by H are put into a class, the classes so obtained combine among themselves by multiplication. In the particular case when H is the group of inner automorphisms we get the classification of the conjugate classes. When H is the total group T of automorphisms some of the conjugate classes are grouped together to form new classes which again combine by multiplication. When G is a cyclic group, a class defined as above by T is composed of all elements of the same order in G. But when G is non-cyclic this is not in general true. For example in the group:

$$P^3 = E, \quad Q^9 = E, \quad PQ = QP$$

there is no automorphism by which P corresponds to Q^3. The question remains, therefore, whether the classes of elements of the same order in a finite group G combine by multiplication or not. The object of the present paper is to show that the classes of elements of the same order combine among themselves by multiplication in an Abelian group and to give the multiplication table of the classes which is analogous to the one given by Dr. R. Vaidyanathaswamy for the cyclic group. Finally we give two simple

* A remarkable property of integers mod N and its bearing on group theory, *Proc. Ind. Acad. Sci.*, A, (1937), **5**, 63.

illustrations to show that such a classification is not possible in a non-Abelian group.

I.

Let G be an Abelian group of finite order N and let the group operation be multiplication.

LEMMA 1. *If* K *is a complex* (*i.e.*) *a set of elements in* G *say* n (K) *in number, then,*

$$K.G = n\,(K).\ G.$$

Proof. Let S be an element in G. The N elements SG are elements in G and no two of them are equal for, if

$$SS_i = SS_j$$
$$S_i = S_j$$
$$\text{therefore, } S.\ G = G.$$

If K contains n (K) elements it then follows that

$$K\ G = n\ (K)\ G.$$

LEMMA 2. *The totality of the elements in* G *whose orders divide a given number* d *form a sub-group* G (d) *of* G.

Proof. If G (d) is the set of all elements in G whose orders divide d, the product of any two elements of the set is an element of the set, for every element the inverse also belongs to the set and the identity element is in the set, hence G (d) is a sub-group of G.

Note.—If g (d, N) is the g.c.d. of d and N, G [g (d, N)] = G (d).

THEOREM 1. *The groups* G (d) *for different divisors* d *of* N *combine among themselves by multiplication.*

Proof. Let d_1 and d_2 be any two divisors of N. We first prove the theorem for,

Case (i) $N = p^a$, (p a prime).

If d_1 and d_2 are divisors of N one (at least) of them is a divisor of the other. Let d_1 be a divisor of d_2 so that G (d_1) is contained in G (d_2) and if m (d_1) is the number of elements in G (d_1)

$$G\ (d_1).\ G(d_2) = m\ (d_1).\ G\ (d_2) \text{ (by Lemma 1), which proves case (i).}$$

Case (ii) $N = p_1^{a_1}\ p_2^{a_2} \cdots p_r^{a_r}$.

In this case G is the direct product of its Sylow sub-groups $G_1, G_2, \ldots G_r$ of orders $p_1^{a_1}, p_2^{a_2}, \ldots p_r^{a_r}$ respectively.

G (d_1) is the direct product of G_1 (d_1), G_2 (d_1), ... G_r (d_1), and G (d_2) is the direct product of G_1 (d_2), G_2 (d_2), ... G_r (d_2).

$$\text{Therefore, } G(d_1).\ G(d_2) = \prod_{\nu=1}^{r} G_\nu(d_1) \cdot G_\nu(d_2).$$

$G_\nu(d_1)$ contains $G_\nu(d_2)$ or *vice versa* according as the elementary block factor† belonging to p_ν is greater or less in d_1 than in d_2. If $g(d_1, d_2)$ is the g.c.d. $l(d_1, d_2)$ is the l.c.m. of d_1 and d_2 and if $m(d)$ represents the number of elements in $G(d)$ we have as in case (i)

$$G(d_1).\ G(d_2) = m[g(d_1, d_2)]\ G[l(d_1, d_2)] \qquad (1)$$

Thus the groups combine by multiplication.

LEMMA 3. *In an Abelian group* G *of order* p^α *and type* $(\alpha_1, \alpha_2, \ldots \alpha_r)$ $(\alpha_1 \geqslant \alpha_2 \geqslant \ldots \geqslant \alpha_r)$.

$$m(p^\beta) = p^{k\beta + \alpha_{k+1} + \cdots + \alpha_r}$$

where k is the number of α's $\geqslant \beta$.

Proof. If $P_1, P_2, \ldots P_r$ is a set of basis elements of G of orders $p^{\alpha_1}, p^{\alpha_2}, \ldots p^{\alpha_r}$ then, $G(p^\beta)$ is generated by

$$P_1^{\pi_1}, P_2^{\pi_2}, \cdots P_k^{\pi_k}, P_{k+1}, \cdots, P_r,$$

where $\pi_s = p^{\alpha_s - \beta}$ $(s = 1, 2 \ldots k)$
and is therefore of order $p^{k\beta + \alpha_{k+1} + \cdots + \alpha_r}$

Cor. If $M(p^\beta)$ denotes the number of elements of order p^β in G then

$$M(p^\beta) = m(p^\beta) - m(p^{\beta-1}) = p^{k(\beta-1) + \alpha_{k+1} + \cdots + \alpha_r}(p^k - 1).$$

THEOREM 2. *If in a finite Abelian group, all elements of the same order are put into a class, the classes so formed combine among themselves by multiplication.*

Proof. Let $C(d)$ denote the class of elements of order d and $M(d)$ represent the number of elements in $C(d)$

$$G(d) = \Sigma C(d')$$

where d' runs through all the divisors of d.

Therefore, $C(d) = \Sigma G(t) \cdot \mu\left(\frac{d}{t}\right)$

summed for all divisors t of d and μ is the Mobiüs function.

Hence, $C(d_i)\ C(d_j) = \left\{\Sigma G(t_i) \cdot \mu\left(\frac{d_i}{t_i}\right)\right\}\left\{\Sigma G(t_j) \cdot \mu\left(\frac{d_j}{t_j}\right)\right\}$

$$= \Sigma\Sigma\, m[g(t_i, t_j)]\ G[l(t_i, t_j)]\ \mu\left(\frac{d_i}{t_i}\right)\mu\left(\frac{d_j}{t_j}\right) \text{ by (1)}$$

summed for all divisors t_i, t_j of d_i, d_j respectively

$$= \Sigma\, \gamma(d_i, d_j, d_k)\ C(d_k),$$

where $\gamma(d_i, d_j, d_k) = \Sigma\Sigma\, m[g(t_i, t_j)]\ \mu\left(\frac{d_i}{t_i}\right)\mu\left(\frac{d_j}{t_j}\right)$

summed for divisors t_i, t_j of d_i, d_j for which $l(d_i, d_j)$ is a multiple of d_k.

$$= M[g(d_i, d_j)] \cdot \Pi\left(1 - \frac{m(p^{a-1})}{M(p^a)}\right) \text{ or } 0$$

† A factor A of B is called a block factor if A is prime to B/A. An elementary block factor is a block factor which is a prime power.

according as the l.c.m. of every two of d_i, d_j, d_k is the same or not and the product extending over the common block factors p^a of d_i, d_j, d_k.‖

By Lemma 3 and its Cor. $\frac{m(p^{a-1})}{M(p^a)}$ may be replaced by $\frac{1}{p^{k(a)}-1}$.

In the case of the cyclic group, if d is a divisor of the order of the group

$$m(d) = d, \quad M(d) = \phi(d)$$

so that $\gamma(d_i, d_j, d_k) = \phi[g(d_i, d_j)] \Pi \left(1 - \frac{1}{p-1}\right)$ or 0 according as the l.c.m. of every two of d_i, d_j, d_k is the same or not and the product extending over the belonging primes of the common elementary block factors of d_i, d_j, d_k. This is easily seen to be equivalent to the formula given by Dr. R. Vaidyanathaswamy.

II.

To illustrate that our Theorem 2 is not true for non-Abelian groups, we can take the group of order 8 defined by

$$P^4 = E, \quad Q^2 = E, \quad PQ = QP^3.$$

The elements of the group may be taken as

$$E, P, P^2, P^3, Q, QP, QP^2, QP^3.$$

Here, P^2, Q, QP, QP^2, QP^3 are elements of order 2 and P, P^3 are elements of order 4.

Now, $(P + P^3)^2 = 2E + 2P^2$

which shows that the classes of elements of the same order do not combine by multiplication.

Again take the symmetric group of degree 5.

Let the conjugate classes corresponding to the partitions

$$1^5, 1^3 2, 1^2 3, 14, 12^2, 23, 5$$

be $C_0, C_1, C_2, C_3, C_4, C_5, C_6$ respectively.

Here, $C_0, (C_1 + C_4), C_2, C_3, C_5, C_6$ are classes of elements of the same order.

We have
$$C_1^2 = 10\,C_0 + 3C_2 + 2C_4$$
$$C_4^2 = 15\,C_0 + 3C_2 + 2C_4 + 5C_6$$
$$C_1 C_4 = 3C_1 + 2C_3 + 3C_5$$

Therefore $(C_1 + C_4)^2 = 25C_0 + 6C_1 + 4C_4 + 6C_2 + 4C_3 + 6C_5 + 5C_6$.

The classes, therefore, do not combine among themselves by multiplication.

I thank Dr. R. Vaidyanathaswamy for his valuable guidance and encouragement in the preparation of this paper.

‖ See my paper "On the multiplicative arithmetic functions connected with a finite Abelian group" to appear shortly in the *Jour. Ind. Math. Soc.*

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part VIII. The Condensations of *o*- and *m*-methoxybenzaldehydes.

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When comparing the yields of the condensation-product of *p*-hydroxybenzaldehyde with those of *p*-methoxybenzaldehyde (*p*-anisaldehyde), attention was drawn to the very high yields in the case of the latter aldehyde, and the need was suggested of making similar comparative studies in the case of salicylaldehyde and its methyl ether.[1]

In the present paper the condensation is described of *o*-methoxybenzaldehyde (*o*-anisaldehyde) with malonic acid. A similar condensation of the *m*-methoxybenzaldehyde (*m*-anisaldehyde) is also described which may be compared with the previously reported condensation of *m*-hydroxybenzaldehyde.[2] It may be stated at once that the general expectation that the yields in the case of the condensations of the methyl ethers will be higher is abundantly fulfilled in both the cases.

For the preparation of *o*-methoxybenzaldehyde, salicylaldehyde was methylated by two different methods, by the method of Hiers and Hager,[3] and by that of Chakravarti, Haworth and Perkin.[4] Both gave good yields, but the latter was quicker and was used for methylating the *m*-hydroxybenzaldehyde also.

By the application of Perkin's reaction to *o*-methoxybenzaldehyde, *i.e.*, by heating the aldehyde (2 parts), anhydrous sodium acetate (1 part) and acetic acid anhydride (3 parts), in a sealed tube at 180° C., for six hours, Perkin obtained *o*-methoxycinnamic acid.[5] Though the melting-point and the other characteristics of the acid are described, the yield is not given. By the application of his own method, *i.e.*, by heating equal weights of the aldehyde and of malonic acid with half their weight of glacial acetic acid, for several hours at 180° C., Stuart obtained *o*-methoxy-benzalmalonic acid, which on further heating gave off carbon dioxide to pass into the cinnamic analogue.[6] Perkin's method has also been again and more recently employed by Posner who continued the heating for nine hours.[7] It does

not appear as if Knoevenagel's reaction has been applied to the condensation of this aldehyde with malonic acid, though the condensation with ethyl malonate in the presence of traces of piperidine is reported by Knoevenagel himself[8] as giving not the corresponding cinnamate but the ethyl *o*-methoxybenzalmalonate.

By carrying out the condensation of the aldehyde with malonic acid under the conditions described below, theoretical yields are obtained in the presence of a trace of either pyridine or α-picoline, within a few hours, and the product is very clean.

In the absence of any base and of any catalyst, the condensation could still take place, but the yield was only about half the theoretical even after six hours' heating. Longer heating improved the yield, but it did not go beyond 90 per cent. It is to be noted that the product was not the *o*-methoxybenzalmalonic acid but the corresponding cinnamic acid as in the other condensations in the presence of traces of organic bases.

Knoevenagel's condensation (*loc. cit.*) of the aldehyde with ethyl malonate in the presence of a trace of piperidine was also tried ; after long heating and long standing, the product was separated, which on hydrolysis with alkali gave a small yield of the methoxycinnamic acid, identified by its melting-point and a mixed melting-point with the pure acid obtained by other methods.

The condensation of the *m*-methoxybenzaldehyde to produce the *m*-methoxycinnamic acid has been very much more studied. As usual the first condensation studied was by the application of Perkin's reaction, which was done by Tiemann and Ludwig.[9] Posner adopted the Knoevenagel's method and heated the aldehyde with malonic acid and alcoholic ammonia at 120° C.[10] The pyridine-piperidine method, first given by Haworth, Perkin and Rankin,[11] later on used by Dutt[12] and modified by Robinson and Shinoda,[13] has been applied recently by Chakravarti, Haworth and Perkin,[4] who using this aldehyde and malonic acid (1 : 3 mols.), in pyridine (3·5 mol.) and a trace of piperidine (5 c.c. piperidine in 250 c.c. pyridine, with 100 g. aldehyde and 160 g. malonic acid), report " an almost quantitative yield " on heating (1·5 hours on a steam-bath and then 15 minutes on a sand-bath). Still more recently, Jones and James have reported having repeated the above condensation—" with pyridine or α-picoline as solvent and piperidine as a catalyst ". The yield is not stated, but may be presumed to be good.[14]

While experiments in our laboratory were in progress, Robinson and Walker have reported a condensation using our method giving more than 90 per cent. yield of the *m*-methoxycinnamic acid,[15] and have confirmed independently the sufficiency and efficiency of the trace of pyridine alone.

From our experiments it is seen that a solvent is not necessary, that high molecular amounts of malonic acid or of pyridine are also unnecessary, and that the organic base in trace is the true catalyst. While very fair or good yields are obtained with other bases, a trace of lutidine is found to give, under the conditions used, over 80 per cent. and a trace of pyridine 100 per cent., yield.

It is remarkable that in this case, no condensation took place in the absence of any organic base, even when the conditions of heating were varied or prolonged. This has also been reported to be the case when the aldehyde was the *m*-hydroxybenzaldehyde.[16]

Experimental.

o-*Methoxybenzaldehyde.*—This was prepared by the two methods referred to above, from salicylaldehyde (Merck's pure synthetic reagent). The fraction boiling between 236° and 244° C. was collected. It became solid when kept in a freezing-mixture, and then melted at 3·5–4·0°C. (compare Perkin, 2·7–3·0°C.)[17]

o-*Methoxycinnamic acid.*—The method of the condensation was the same as before. The aldehyde (2·7 g.) and the malonic acid (2 g.) were taken each time, with 0·15 mole. of the organic base. Water-bath was used for the heating and 4–5 hours on it were sufficient. The yields were as under :—

Name of the base	Yield, weight	Yield %	Heating
Pyridine ..	3·55	100	4-5 hours
α-Picoline ..	3·55	100	,,
Lutidine ..	3·0	84	,,
Quinoline ..	2·1	59	,,
Piperidine ..	2·1	59	,,
No Base ..	1·7	48	6 hours
,, ..	3·2	90	12 hours
,, ..	3·2	90	18 hours

The acid was slightly and differently coloured as obtained in all the above condensations, except when pyridine was used, when it was colourless, and melted at 184–185° C. (182–183°, Perkin, *loc. cit.*; 183–184°, Pschorr and Einbeck,[18]; 185–186°, Reychler,[19]; 184–185°, Weerman,[20]).

Condensation with ethyl malonate.—Experiments were simultaneously made in several different lots, in all cases traces of piperidine being used. One lot kept at the ordinary laboratory temperature for several weeks did not show any visible change, but when a portion of it was hydrolysed by 20 per cent. KOH and then acidified with HCl, it gave the *o*-methoxycinnamic acid. Other experiments to shorten the time by applying heat for a part of the period, did not very well succeed. This subject was not pursued further, because the ethyl *o*-methoxycinnamate could be expected to be obtainable from the aldehyde in a much shorter time by Claisen's method[21] as applied by Reychler,[22] who reports good yields from anisaldehyde and piperonal.

m-*Methoxycinnamic acid.*—The *m*-methoxybenzaldehyde was prepared from *m*-hydroxybenzaldehyde as stated above. It boiled at 230° C. It was condensed with malonic acid in the usual manner the details being the same as in the case of the *o*-isomer. The yields were as under :—

Name of the base	Yield, grams.	Yield %	Heating
Pyridine ..	3·55	100	6 hours
Lutidine ..	3·2	90	,,
α-Picoline ..	3·2	90	,,
Piperidine ..	2·1	62	,,
Quinoline ..	2·0	56	,,
No base ..	0·0	0	6 to 18 hours

The acid obtained from the condensation carried out in the presence of pyridine was colourless, and on recrystallisation melted at 117°. (Tiemann and Ludwig, 115°; Posner, 117°, *loc. cit.*)

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TAUTOMERISM OF 2-PHENYL-3-CARBETHOXY-4-HYDROXY-QUINOLINE.

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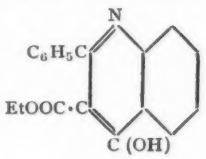
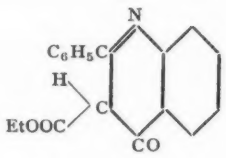
In continuation of the authors' work on 2-phenyl-4-hydroxy-3-carbethoxy-quinolines,[1] several reactions of the rarely studied 2-phenyl-3-carbethoxy-4-hydroxy-quinoline[2] now available in quantity through the authors' improved method, have been investigated.

In literature, the quinoline derivative has been assigned the structure of a hydroxy-quinoline ; it is now shown that it reacts in the enolic form (I) as well as in the ketonic form (II).



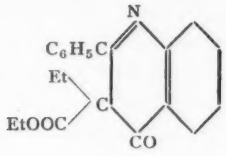
(I)



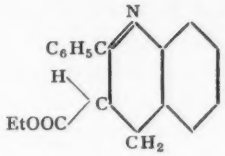
(II)

The quinoline derivative neither gives colouration with alcoholic $FeCl_3$ nor absorbs bromine ; hence it appears that the compound normally has the structure (II). Ethylation with ethyl iodide and sodium ethoxide gives an ethyl derivative which was proved to be the C-ethyl compound (III), as it is identical with the C-ethyl derivative synthesised from benzanilide-imidochloride and C-ethyl malonic ester according to the authors' method.[1] The corresponding C-methyl derivative has also been obtained whose constitution has been assigned from its analogy with the C-ethyl homologue. The formation of C-ethyl derivative shows that the compound reacts in the ketonic form (II).

Clemmensen reduction[3] of the quinoline derivative affords 2-phenyl 3 : 4-dihydro-3-carbethoxy-quinoline (IV) further showing that the compound reacts in the ketonic form (II).



(III)

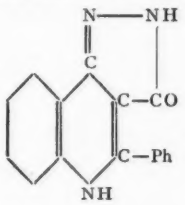


(IV)

The quinoline derivative however does not form the phenyl hydrazone, semi-carbazone, or oxime.

The quinoline derivative reacts with phosphorus pentachloride in the enolic form (I) forming 2-phenyl-3-carbethoxy-4-chloro-quinoline ; the mobility of the Cl atom in the chloro-quinoline manifests itself by its reaction with aqueous alcoholic NaOH ; it yields 2-phenyl-4-hydroxy-quinoline-3-carboxylic acid.

Seka and Fuchs[2] obtained by the action of phosphorus pentachloride, a chloro-derivative which on treatment with ammonia and hydrazine yielded respectively 4-hydroxy-2-phenyl-quinoline-3-carboxylamide and a compound to which they assigned the constitution (V).



(V)

It is interesting to note that although 2-phenyl-3-carbethoxy-4-hydroxy-quinoline normally has the ketonic structure, the corresponding carboxylic acid gives slight colouration with alcoholic $FeCl_3$, and the decarboxylated compound 2-phenyl-4-hydroxy-quinoline now prepared by an improved method, gives a strong colouration with alcoholic $FeCl_3$, and also decolourizes bromine showing that it is enolic in constitution.

On reduction with tin and hydrochloric acid, the quinoline derivative gave a compound of the probable formula 2-phenyl-3-carbethoxy-4-hydroxy-tetrahydro-quinoline ; the carbethoxy-quinoline forms an acid sulphate and picrate ; it does not form a methiodide probably due to stearic hindrance of the phenyl group in the 2-position.

Experimental.

(i) 2-*Phenyl*-3 : 4-*dihydro*-3-*ethyl*-3-*carbethoxy*-4-*quinolone*.—A mixture of 2-phenyl-3-carbethoxy-4-hydroxy-quinoline (2 g.) (1 mol.), sodium ethylate

prepared from sodium (0·35 g.) (2 atoms), and EtI was refluxed in absolute alcohol for 4 hours, evaporated to dryness, and treated with water; a semi-solid mass was obtained which solidified on standing; it crystallises from alcohol in tiny needles, m.p. 226–228°; yield 1 g. (45·5%).

[Found: N, 4·6%; $C_{20}H_{19}O_3N$ requires N, 4·4%.]

It is insoluble in cold and soluble in hot methyl and ethyl alcohols and acetone; it is insoluble in cold and hot chloroform, benzene, toluene and petroleum ether.

(ii) The compound was synthesised according to the authors' improved method[1] from benzanilide-imidochloride (4 g.) (1 mol.), sodium (0·5 g.) (1 atom), and ethyl malonic ester (7 g.) (2 mols.); the crude oily condensation product obtained was heated at 180–190° till the evolution of bubbles of ethyl alcohol ceased. The crude product obtained in the form of an oily mass was treated with ethyl alcohol when the quinoline derivative crystallised in needles, m.p. 227–228°; mixed m.p. with the compound (i) showed no depression; yield 1·5 g.

2-*Phenyl*-3 : 4-*dihydro*-3-*methyl*-3-*carbethoxy*-4-*quinolone*.—It was prepared in the same way as the corresponding ethyl compound from the quinoline derivative (6 g.) (1 mol.), sodium (1 g.) (2 atoms) and excess of MeI. It was obtained as an oily product which solidified on standing. It crystallises from methyl alcohol in needles, m.p. 164–166°; yield 3·5 g. (55·5%).

[Found: N, 4·8%; $C_{19}H_{17}O_3N$ requires N, 4·6%.]

It is sparingly soluble in cold and easily in hot methyl and ethyl alcohols, and acetone; it is difficultly soluble in hot benzene, toluene and chloroform.

2-*Phenyl*-3 : 4-*dihydro*-3-*methyl*-3-*carboxy*-4-*quinolone*.—It was prepared by hydrolysis of the quinoline-ester (1 g.) with hot aqueous alcoholic NaOH. It crystallises from ethyl alcohol in needles, m.p. 221–222° with evolution of CO_2; yield 0·3 g.

[Found: N, 5·3%; $C_{17}H_{13}O_3N$ requires N, 5·0%.]

2-*Phenyl*-3 : 4-*dihydro*-3-*carbethoxy*-*quinoline*.—The quinoline derivative was reduced by improved Clemmensen's method.[3]

Zinc dust (Merck's) (20 g.) was suspended in 20 c.c. 5% $HgCl_2$ solution and left overnight; the next day it was washed twice with HCl (1 : 1), and the quinoline derivative (2 g.) suspended in alcohol was added to it; the mixture was refluxed for 5–6 hours; at intervals of one hour 5 c.c. HCl (conc.) was added; the reduction product separated as an oil, and was purified by two crystallisations from aqueous alcohol; it is a pale yellow crystalline solid decomposing at 125°; yield 0.2 g.

[Found : C, 76·2%; H, 6·1%; N, 5·0%; $C_{18}H_{17}O_2N$ requires C, 77·4%; H, 6·1%; N, 5·0%.]

2-Phenyl-3-carbethoxy-4-chloro-quinoline.—The reaction with phosphorus pentachloride was carried out in dry chloroform, toluene, $POCl_3$, and without the use of any solvent; it was found that best results were obtained with toluene as solvent.

The quinoline derivative (7 g.) (1 mol.) and PCl_5 (49 g.) (1 mol.) were refluxed in anhydrous toluene till HCl gas was evolved, treated with ice and extracted with ether; ether and toluene were removed; the residual product crystallised on standing; it crystallises from toluene in prismatic needles, m.p. 101–103°; yield 6 g. (53·5%).

[Found : Cl, 11·6%; $C_{18}H_{14}O_2NCl$ requires Cl, 11·4%.]

2-Phenyl-3-carbethoxy-4-hydroxy-tetrahydro-quinoline.—The quinoline derivative (5 g.) dissolved in alcoholic HCl was refluxed with tin for 4–5 hours when a crystalline solid separated; it crystallises from aqueous alcohol in tiny needles, melting at 245°; yield 1 g.

[Found : C, 72·7%; H, 5·9; $C_{18}H_{19}O_3N$ requires C, 72·7%; H, 6·4%.]

The acid sulphate.—The quinoline derivative (1 g.) dissolved in hot alcohol was treated with dilute H_2SO_4; crystals of the sulphate, m.p. 212–215° separated from the solution on cooling; yield 0·5 g.

[Found : N, 3·9%; $C_{18}H_{17}O_7NS$ requires N, 3·6%.]

The picrate.—The quinoline derivative (0·3 g.) and picric acid were refluxed in alcohol for three hours; on cooling crystals of the picrate separated, m.p. 247–250°; yield 0·1 g.

[Found : N, 10·8%; $C_{24}H_{18}O_{10}N_4$ requires N, 10·7%.]

Decarboxylation of 2-phenyl-4-hydroxy-quinoline-3-carboxylic acid.—The carboxylic acid (0·5 g.) was heated with 25 c.c. water in a sealed tube at 210–220° for six hours; 2-phenyl-4-hydroxy-quinoline forms glistening plates, m.p. 251–253° (Just[2] gives m.p. 254°); yield 0·4 g. (95%).

[Found : N, 6·4%; calc. for $C_{15}H_{11}ON$, N, 6·3%.]

The analyses recorded were carried out by Dr. Schoeller of Berlin.

Summary.

In this paper, tautomerism of 2-phenyl-3-carbethoxy-4-hydroxy-quinoline has been investigated.

The quinoline derivative neither gives colouration with alcoholic $FeCl_3$, nor absorbs bromine showing thereby that normally it has the ketonic structure. The formation of C-alkyl derivatives also show that the

compound reacts in the ketonic form. Clemmensen reduction affords 2-phenyl-3 : 4-dihydro-3-carbethoxy-quinoline.

The quinoline derivative, however, reacts with phosphorus pentachloride in the enolic form forming 2-phenyl-3-carbethoxy-4-chloro-quinoline.

It is interesting to note that although 2-phenyl-3-carbethoxy-4-hydroxy-quinoline normally has the ketonic structure, the corresponding quinoline-carboxylic acid shows slight colouration with alcoholic $FeCl_3$, and 2-phenyl-4-hydroxy-quinoline which has now been obtained by an improved method gives a strong colouration with alcoholic $FeCl_3$ and also absorbs bromine showing that it is enolic in constitution.

On reduction with tin and hydrochloric acid, the quinoline derivative forms 2-phenyl-3-carbethoxy-4-hydroxy-tetrahydro-quinoline ; it also forms an acid sulphate and picrate.

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THE RAMAN SPECTRA OF CRYSTAL POWDERS.

V. Inorganic Nitrates : Water of Crystallisation.

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Introduction.

In a recent note in *Current Science*, the author (1937) reported certain new results furnished by the application of the technique of complementary filters to the study of the Raman spectra of crystalline nitrates. It was also mentioned in that connection that the Raman spectrum of the water of crystallisation present in many of these salts, shows peculiar and interesting changes from substance to substance. It is proposed to deal with these questions at somewhat greater length in the present paper.

Part I—Nitrates.

The inorganic nitrates furnish a class of compounds whose Raman spectra both as solids and as aqueous solutions have been extensively studied. The nitrates of some of the alkali metals have also been examined in the fused state.

Menzies (1929) and Bär (1929) were the first to apply the powder technique to the study of the Raman spectra of crystalline nitrates. For crystalline KNO_3, Menzies obtained a single Raman line at 1052 cm.$^{-1}$ Bär found the frequencies 706 and 1056 for NH_4NO_3, 1074 for $NaNO_3$ and 1054 for calcium nitrate.

Krishnamurti (1930) investigated by the powder technique the spectra of some eighteen nitrates, some as anhydrous and others as hydrated crystals. In the series of salts examined by him, he found that the most intense Raman line which is an inactive frequency of the nitrate ion showed frequency changes extending over the range 1030 to 1066 cm.$^{-1}$ He tried to interpret this variation as the influence of the cation on the vibrations of the $(NO_3)^-$ ion. Besides this line, two others of lesser intensity, originating presumably from the internal vibrations of the $(NO_3)^-$ ion were observed in the spectra of certain nitrates. The frequency shifts of these lines were in the neighbourhood of 720 and 1360 cm.$^{-1}$ respectively.

Gerlach (1930) studied the Raman spectra of a few nitrates and found that the inactive frequency of the nitrate ion showed a dependence upon the crystal structure, water of crystallisation and nature of the cation.

Nisi (1933) examined the Raman spectra of $NaNO_3$, KNO_3, NH_4NO_3, $RbNO_3$ and $CsNO_3$, using single crystals of these substances. Barring the low frequency lattice oscillations, the spectra of all these substances showed in general an intense line whose frequency shift was about 1050 wave numbers, and two less intense lines near 720 and 1360 cm.$^{-1}$ respectively. The 1360 line was, however, found to be absent in the spectrum of NH_4NO_3. In addition to the three frequencies mentioned above, the spectrum of $NaNO_3$ showed also a fourth frequency 1666 cm.$^{-1}$

Raman spectra of aqueous solutions of nitrates have been studied by Grassmann (1932), Silveira (1932), Silveira and Bauer (1932), Nisi (1933), and Ollano and Frongia (1933). Grassmann noticed that the intense Raman line near 1050 cm.$^{-1}$ which is sharp in the spectra of crystalline nitrates, is somewhat broad in the spectra of their aqueous solutions. The frequency near 720 cm.$^{-1}$ was found to be split up into two diffuse components 715 and 740, in the aqueous solutions of calcium and cadmium nitrates, but no observable splitting was noticed in the spectra of solutions of lithium, ammonium, sodium, silver, magnesium and lead nitrates. The relative intensities of the components altered with the concentration of the solution. Grassmann also found that the Raman line at 1050 cm.$^{-1}$ is highly polarised, while 720 is depolarised ($\rho \approx \frac{6}{7}$). The spectra of the nitrates of potassium and lithium were also studied by him in the fused state; the spectra of the fused salts did not differ essentially from those of their respective solutions.

Solutions of $Cu(NO_3)_2$ investigated by Silveira showed a splitting of the two frequencies near 720 and 1360 cm.$^{-1}$ respectively, into two components—717 and 754 in the case of the former, and 1325 and 1421 in the case of the latter. A diffuse band at 1654 cm.$^{-1}$ observed in the spectrum of the solution was attributed to water. Silveira and Bauer studied the Raman spectra of aqueous solutions of calcium and magnesium nitrates. In conformity with Grassmann's results, they found a splitting of the 720 frequency in the case of $Ca(NO_3)_2$, but not in the case of $Mg(NO_3)_2$. Besides the strong Raman line at 1052 cm.$^{-1}$, they found three bands 1346, 1427 and 1655 cm.$^{-1}$ for $Mg(NO_3)_2$, and 1346, 1439 and 1659 for $Ca(NO_3)_2$. Since the 1650 band was also present in the spectra of aqueous solutions of a number of other salts such as $CaCl_2$, $SrCl_2$, $MgCl_2$, etc., they concluded that this band originated from the vibrations of the water molecules.

Nisi's work on the Raman spectra of aqueous solutions of sodium, potassium, ammonium and calcium nitrates showed that the frequency shift of the most intense Raman line is very nearly constant in all these cases. This was also the conclusion arrived at earlier by Grassmann who had noticed that while in concentrated solutions of nitrates the position of this line depended upon the concentration as well as upon the nature of the cation, with progressive dilution this frequency approached a constant limiting value $\Delta\nu = 1048 \pm 1$ cm.$^{-1}$ In the spectra of the solutions of the alkali nitrates, the 720 frequency appeared as single while it was split up into two components 715 and 740 in the solution of $Ca(NO_3)_2$. In concentrated solution (15 normal), 740 was more intense than 715; in dilute solutions (5 normal), there was a reversal in the relative intensities of the components which had at the same time become considerably diffuse. Besides these frequencies, three other diffuse Raman bands were observed in the spectra of aqueous solutions of all the four nitrates examined by Nisi. These had approximately the following frequency shifts:—

$NaNO_3$	1357, 1414, 1663 cm.$^{-1}$
KNO_3	1349, 1413, 1659
NH_4NO_3	1332, 1374, 1659
$Ca(NO_3)_2$	1350, 1440, 1650

Since Nisi could not find even a trace of the 1650 band in the spectrum of pure water, he considered it extremely doubtful whether it had its origin in the water molecules.

It is generally believed that the $(NO_3)^-$ ion has a planar symmetric configuration with the three oxygen atoms at the corners of an equilateral triangle and the nitrogen atom at the centre. The symmetry of the ion is then D_{3h}. It will have four fundamental vibrations:—

(i) the totally symmetric vibration, inactive in the infra-red but active and generally very intense in the Raman effect;

(ii) the perpendicular vibration which is forbidden in the Raman effect but allowed in the infra-red;

(iii) & (iv) two doubly degenerate vibrations, allowed in the Raman effect as well as in the infra-red.

The infra-red absorption spectrum of $NaNO_3$ has been examined by Schaefer and his collaborators (1930). Absorption maxima were found in the neighbourhood of 830, 720 and 1360 cm.$^{-1}$ Considered in conjunction with the Raman spectrum of this substance, one might conclude that 1050 and 830 are respectively the totally symmetric and perpendicular vibrations of the $(NO_3)^-$ ion, while 720 and 1360 are the two doubly degenerate

vibrations. The state of polarisation of the Raman lines 1050 and 720 also supports this assignment.

There are, however, a number of points relating to the Raman spectra of nitrates that await explanation and experimental elucidation. In the first place, we have to inquire as to whether the degenerate vibrations are single in the crystalline nitrates of all metals, and if so as to why they split up in aqueous solution. It is again a point for inquiry as to why the degenerate vibrations show a dependence on the nature of the cation in aqueous solutions, while the totally symmetric vibration, to a first approximation, does not. We have also to decide whether the 1650 band observed in aqueous solutions of nitrates arises from the $(NO_3)^-$ ions or from the water molecules. A detailed experimental investigation of the Raman spectra of a large number of crystalline nitrates is an essential preliminary towards the understanding of these questions. The results of earlier investigators in this respect are very incomplete indeed, because the powder technique employed by them enabled them to record only the strongest Raman line near 1050 cm.$^{-1}$ in the case of by far the majority of nitrates studied. Also, as we shall see, even the work with single crystals has not enabled Nisi to record all the vibrational frequencies of the $(NO_3)^-$ ion in the salts studied by him. The present author has repeatedly pointed out that the technique of complementary filters described by him (1937) enables one to record even the faintest Raman lines in the spectra of crystal powders. The Raman spectra of the following eleven nitrates $NaNO_3$, KNO_3, NH_4NO_3, $Pb(NO_3)_2$, $Sr(NO_3)_2.4H_2O$, $Ca(NO_3)_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $Mg(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Ce(NO_3)_3.6H_2O$, and $Bi(NO_3)_3.5H_2O$, have therefore been re-investigated by this method. The substances examined comprise the nitrates of mono-, bi- and tri-valent metals. The first four nitrates are anhydrous while the remaining seven are hydrated crystals.

Experimental.

All the nitrates employed in the investigations were either Kahlbaum's or Merck's purest salts. The spectra of the crystals were photographed on a Hilger two-prism spectrograph of high light-gathering power. λ 4046 was the exciting line in all cases. The time of exposure varied from 48 to 72 hours, using Ilford "Golden Iso-zenith" plates. The frequency shifts were estimated by measuring the plates on a Hilger wavelength micrometer with iron arc comparison.

Results.

The results are given in the following tables. The intensity of the strongest Raman line near 1050 cm.$^{-1}$ is arbitrarily assumed as 12 in all

those cases in which it is not split up. In the spectra of all the nitrates, this line was present both by λ 4046 and by λ 4078 excitations. The two frequency shifts differed in no case by more than one wave number, and their mean value is given in the tables. The frequency shifts of the water bands in the 3 μ region observed in the spectra of the hydrated salts are not included in the tables. These will be dealt with in the second part of the paper.

1. $NaNO_3$.

Author	723 2	1069 12	1385 6	..
Krishnamurti	719·7	1066	1383·1	..
Cabannes and Canals ..	730·4	1074·2	1391·4	1678·5
Schaefer, Mattosi, Aderhold ..	729·3	1069·4	1385·6	1665·4
Nisi	722.6 *m*	1067·5 *v.st*	1385·2 *st*	1666·3 *v.f*

2. KNO_3.

Author	715 2	1050.5 12	1343 3	1360 3
Krishnamurti	711·3	1051.1	1350.5	
Nisi	710·9 *f*	1048.3 *st.*	1344.2 *m*	

3. NH_4NO_3.

Author ..	716 2	1051 12	1291 0*b*	1360 1*b*	1423 ½*b*	1455 0*b*		3150 5*v,bd*
Krishnamurti	709.3	1043						
Nisi ..	714.4 *f*	1041.5 *st*					1869 *f.d*	

4. $Pb(NO_3)_2$.

Author ..	730 ½	1048·5 12		1420 ½	1537 1	1614 2	1645? ½
Krishnamurti	728	1046·8	1382				

5. $Sr(NO_3)_2.4H_2O$.

Author ..	742 4	1058.5 12	1369 1	1400 2	1421 2	1537 0	1635 1
Krishnamurti	733	1056.5					

6. $Cd(NO_3)_2.4H_2O$.

Author ..	743 ½	1055 12	1331 ½*d*	1456 2*bd*	1536 0	Water-band
Krishnamurti		1051				

7. $Ca(NO_3)_2.4H_2O$.

Author ..	745 1	1050.5 12	1360 3*b*	1424 3*b*	1537 ½	Water-band
Krishnamurti		1047.0				

8. $Mg(NO_3)_2.6H_2O$.

Author ..	720 0	1056 12	1355 1*b*	1424 3*b*	1505 0	Water-band
Krishmanurti		1047				

9. $Cu(NO_3)_2.3H_2O$.

Author ..	718 ½	756 1	1020 6	1048 10	1285 2	1325 1	1430 1*b*	1500 4*b*	Water-band

10. $Ce(NO_3)_3.6H_2O$.

Author ..	736 ½	1043 8	1053 8	1350 1*d*	1455 3*bd*	1540? 0	1640 ? 0	Water-band

11. $Bi(NO_3)_3.5H_2O$.

Author ..	720 ½	750 1	1036 12	1285 0	1302 ½*b*	1440 2*b*	1486 6*b*	1536 ½	1625 1*b*	Water-band
Krishnamurti			1037							

Discussion of Results.

$NaNO_3$ and KNO_3.—Crystals of sodium and potassium nitrates are isomorphous with calcite and aragonite respectively. Hence, a comparative study of their Raman spectra is of great interest. Three Raman lines 723, 1069 and 1385 have been observed in the spectrum of $NaNO_3$, of which 1069 is the most and 723 the least intense. All the three lines are characterised by extreme sharpness. As can be seen from the preceding section, the Raman spectrum of crystalline $NaNO_3$ has been examined by a number of previous investigators. The author's results show the best agreement with those of Nisi. Since only λ 4046 excitation was employed in the present investigation, the fourth frequency near 1665 cm.$^{-1}$ observed by Cabannes, Schaefer and Nisi in the spectrum of $NaNO_3$ crystals, could not be observed in the present case because of its overlapping with the λ 4358 group of mercury lines.

In contrast to the observations of Krishnamurti and Nisi, the Raman spectrum of KNO_3 reported here differs essentially from that of $NaNO_3$. In place of the single sharp line at 1385 observed in the case of $NaNO_3$, we find a pair of sharp lines 1343 and 1360 in the spectrum of KNO_3. These two lines are of equal intensity, and their aggregate intensity is comparable with that of the 1385 line of $NaNO_3$. We have here a typical instance of the influence of crystal structure on the vibrations of the $(NO_3)^-$ ion.

It is of interest in this connection to compare the Raman spectra of sodium and potassium nitrates with the spectra of calcite and aragonite respectively. Since the $(CO_3)^{--}$ and $(NO_3)^-$ ions are supposed to have a similar structure, we should expect a corresponding parallelism between their Raman spectra. Nisi (1933) has recorded the following frequencies for the $(CO_3)^{--}$ ion in the case of calcite and aragonite, using single crystals of these substances :

Calcite	..	712·5	1085·5	1434·3	1753·3
		m	*v. st*	*f*	*v f*
Aragonite	..	701	1085	..	..
		m	*st*		

The frequency corresponding to the 1434 line of calcite has not been observed by Nisi in the spectrum of aragonite. On the analogy with the alkali nitrates, however, it is probable that this frequency will be a doublet in the case of aragonite. The author hopes to examine shortly the Raman spectra of these two substances by the technique of complementary filters.

The totally symmetric vibration of the $(CO_3)^{--}$ ion has practically the same frequency (1085 cm.$^{-1}$) in the spectra of calcite and aragonite ; the

corresponding frequency of the $(NO_3)^-$ ion is 1069 for $NaNO_3$ and 1051 for KNO_3. This difference is presumably due to the influence of the cation on the vibrations of the nitrate ion. The exact nature of this influence is not clear, but it might in general be expected to depend also on the crystal form.

NH_4NO_3.—Ammonium nitrate exhibits the phenomenon of polymorphism to a remarkable degree. It exists in about five different crystalline modifications depending upon temperature. At room temperature, the crystal structure is orthorhombic, so that it is isomorphous with KNO_3. In addition to the frequencies 715 and 1050 also recorded by Nisi and Krishanmurti, four faint lines 1291, 1360, 1423 and 1455 and a strong band at 3150 cm.$^{-1}$ have been observed in the spectrum of this substance. The 3150 Raman band as well as one of the frequencies in the 1400 region has to be attributed to the $(NH_4)^+$ ion. The Raman spectrum of the $(NH_4)^+$ ion in ammonium nitrate is different from the spectra of NH_4Cl and NH_4Br recently discussed by the author (1937). The frequency of the $(NO_3)^-$ ion near 1360 is split up into two or more components in crystalline NH_4NO_3. The faint line at 1869 reported by Nisi was not observed.

$Pb(NO_3)_2$.—Unlike the majority of the nitrates of bivalent metals, lead nitrate crystallises without water of crystallisation. In common with a large number of anhydrous nitrates of the type $M(NO_3)_2$, lead nitrate is found by X-ray crystal analysis to possess the cubic structure at room temperature. This very probably means that the nitrate group has spherical symmetry at room temperature in the crystal lattice of all these nitrates.

Compared with the Raman spectra of sodium and potassium nitrates, the spectrum of $Pb(NO_3)_2$ presents a great contrast. The most intense line at 1048·5 is only 2 wave numbers less than the corresponding frequency of KNO_3. In the 720 region only a very faint line is present. A series of four lines 1420, 1537, 1614 and 1645 are also found in the spectrum of $Pb(NO_3)_2$, 1614 being the most intense. The frequency 1382 reported by Krishnamurti was absent on the author's plates. The spectrum of the substance, however, showed an appreciable background which might have masked fainter lines.

$Sr(NO_3)_2.4H_2O$.—The frequency 742 cm.$^{-1}$ is relatively very intense in the spectrum of this substance. A number of frequencies are observed between 1300 and 1650 wave numbers. Although the substance was taken from a bottle labelled ' Kahlbaum, $Sr(NO_3)_2.4H_2O$ ' the water-bands in the 3 μ region were not recorded. It is probable that the sample investigated was the anhydrous salt.

$Cd(NO_3)_2.4H_2O$ and $Ca(NO_3)_2.4H_2O$.—The spectra of these two substances differ strikingly in the region above 1300 wave numbers. Of the

two frequencies 1331 and 1456 in the spectrum of cadmium nitrate, the first is a faint and diffuse line while the other is a broad and diffuse band of much greater intensity. The corresponding lines 1360 and 1424 of calcium nitrate are practically of the same intensity and structure. The water bands are clearly recorded in the spectra of both these salts.

$Mg(NO_3)_2.6H_2O$.—The Raman spectrum in this case consists of two sharp lines 720 (0) and 1056 (12), and three broad ones 1355 (1*b*), 1424 (3*b*), and 1505 (0). On account of the very long exposures, the spectra of all the nitrates showed an appreciable background over a region extending up to about 800 wave numbers from the exciting line. Consequently, very faint lines in this region, if present, might have escaped notice. The water-bands were strongly recorded in the spectrum.

$Cu(NO_3)_2.3H_2O$.—The spectrum in this case is characterised by extreme complexity, and shows as many as eight distinct frequencies. In place of the single sharp line near 1050 cm.$^{-1}$, two sharp and strong lines (1020 and 1048) of unequal intensity are observed. It is extremely doubtful whether a single molecular or ionic configuration can explain all the observed frequencies, since even in the complete absence of all symmetry elements, the $(NO_3)^-$ ion will have only six characteristic frequencies.

$Ce(NO_3)_3.6H_2O$ *and* $Bi(NO_3)_3.5H_2O$.—The main nitrate line is split up into two components of equal intensity in the spectrum of cerous nitrate. The frequency shifts of the two components are 1043 and 1053 respectively. In the case of bismuth nitrate, the corresponding line is single, but has a wing-like structure towards the side of the exciting line. The spectrum of bismuth nitrate shows eight other frequencies, of which the one at 1486 is particularly intense. Even in this case, it is difficult to understand the existence of so many frequencies with a single ionic configuration.

Some General Conclusions.

The results of the present investigation show quite decisively that while the Raman spectra of sodium and potassium nitrates are relatively simple, the spectra of the nitrates of the bi- and tri-valent metals are generally characterised by an increasing degree of complexity. The frequency corresponding to the infra-red absorption in the neighbourhood of 830 cm.$^{-1}$ is absent in the spectra of all the nitrates examined by the author. The Raman line near 1050 cm.$^{-1}$ is generally very intense and sharp in the spectra of all the nitrates. In the spectra of $Cu(NO_3)_2.3H_2O$ and $Ce(NO_3)_3.6H_2O$, it is split up into two components whose separation and relative intensities are different in the two cases. The 720 region generally shows one or two *sharp* lines which are very much less intense compared with the main nitrate

frequency near 1050. The frequency shift of this line lies somewhere between 710 and 745 cm.$^{-1}$, depending upon the particular nitrate; its intensity varies from one nitrate to another. Among the substances examined in the present work, this frequency is most intense in the spectrum of strontium nitrate.

The frequency interval between 1100 and 1600 cm.$^{-1}$ is found to be one of extreme complexity in the spectra of the nitrates of bi- and tri-valent metals. Except in the case of the nitrates of the alkali metals sodium and potassium, the Raman lines observed in this region are more or less broad and diffuse. The number of Raman lines in this region, their structure, frequency shifts, relative intensities, etc., show the most surprising variations from one nitrate to another. Excepting crystalline $NaNO_3$, the spectra of all the nitrates examined here show two or more frequencies in this region. Frequencies above 1600 cm.$^{-1}$ have been found to be definitely present in the spectra of $Pb(NO_3)_2$, $Sr(NO_3)_2.4H_2O$ and $Bi(NO_3)_3.5H_2O$. It is probable that such frequencies are present in the spectra of some of the other nitrates as well, but have not been observed in the present investigation because of their superposition with the λ 4358 group of mercury lines.

We thus see that the Raman spectrum of the nitrate ion in crystalline inorganic nitrates shows profound changes depending upon the crystal structure, nature of the cation, and presumably also on the number of molecules of water of crystallisation. Further investigation is, of course, necessary before one can understand the exact significance of all these results revealed by the application of the new technique, but it is interesting to note that the two bands near 1350 and 1440 cm.$^{-1}$ observed by several previous investigators in the spectra of aqueous solutions of nitrates have their analogues in the crystal spectra of *hydrated* calcium and magnesium nitrates.

Part II—Water of Crystallisation.

By far the majority of salts crystallise from aqueous solutions in combination with a definite number of molecules of water—known as water of crystallisation—per molecule of the substance. It is generally, though not always, possible to remove these water molecules without bringing about the decomposition of the substance, and subsequently to restore them by re-crystallisation from water. The degree of hydration—the number of water molecules taken up by each molecule of the salt—depends upon the nature of the anion and the cation. Like water and ice, the hydrates have a definite vapour pressure which increases in a regular manner as the temperature rises.

Although we have an immense mass of physico-chemical data relating to the composition, stability, conditions of formation, etc., of hydrates, our knowledge of the nature of the forces that come into operation in their formation is as yet very unsatisfactory. Since we know that salts are generally ionised even in the solid state, the water molecules must be assumed to be attached in some manner either to the cation or to the anion. The electrostatic theory of Born (1920) assumes that the water molecules which are electrical dipoles are retained by the electrostatic attraction of the ions. On the other hand, there is the Co-ordination Theory of Werner expounded and elaborated by Sidgwick (1927), according to which, each water molecule is supposed to be bound by means of a co-ordinate link either to the positive or to the negative ion. According to Sidgwick, the oxygen of the water molecule acts as the " donor " when a co-ordinate link is established between it and a cation :

$$X^+ + H_2O = \left[X \leftarrow O\begin{matrix}H\\H\end{matrix}\right]^+$$

while one of the H atoms of the water molecule acts as the " acceptor " when it forms a co-ordinate link with an anion :

$$A^- + H_2O = [A \rightarrow H\text{–}O\text{–}H]^-$$

On account of the greater co-ordinating power of the oxygen in water, it is to be expected that the hydration of cations is of more frequent occurrence.

The co-ordination theory successfully explains a large number of facts, although little is known about the mechanism of the co-ordinate electron-sharing link. In a series of papers, Garrick (1930, 1931, 1932) has tried to show that the electrostatic theory also leads to results which agree satisfactorily with observation.

Day, Hughes, Ingold and Wilson (1934) attempted to test the rival theories of ionic hydration by the use of heavy water. On account of the appreciable differences in the physical properties of H_2O and D_2O, it was expected that on the basis of the structural theory, fractionation should occur when salts which form hydrates are crystallised from water with a known percentage of deuterium content. However, the observed results in a large number of cases were in the negative.

The Raman spectra of crystalline hydrates might be expected to throw some light on the question of the nature of crystal water, since the vibrations of the water molecules are bound to be more or less modified by the crystalline environment. Although the literature on the Raman spectrum of liquid water is voluminous, the spectral characters of crystal water are

only very incompletely known. This is because of the technical difficulties hitherto experienced in the photography of the Raman spectra of crystalline substances not easily accessible in the form of large single crystals. Perhaps, the only systematic investigation of the Raman spectra of water of crystallisation is that of Nisi (1931) in the case of a number of sulphates using single crystals. Most of these crystals showed a single diffuse band whose frequency shift was round about 3240 cm.$^{-1}$ $CuSO_4.5H_2O$ showed a triple water-band, the components being approximately at 3211, 3377 and 3497 cm.$^{-1}$ Gypsum, $CaSO_4.2H_2O$, gave two sharp water-bands 3404 and 3497, the relative intensities of which varied markedly with the directions of observations and illumination.

The technique of complementary filters is especially suited for the study of the water-bands in the case of hydrated crystals since the water-band excited by λ 4046 falls in a region of the plate which is exceptionally clear and very sensitive. A thorough and systematic study of the behaviour of the water of crystallisation in Raman effect is thus rendered possible for the first time, and the present paper contains the results of such a study in the case of the following fourteen substances :—

$Mg(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, $Ce(NO_3)_3.6H_2O$, $Bi(NO_3)_3.5H_2O$, $SrCl_2.6H_2O$, $MgCl_2.6H_2O$, $MnCl_2.4H_2O$, $CuSO_4.5H_2O$, $Na_3VO_4.12H_2O$, $Na_3PO_4.12H_2O$, $Na_2CO_3.10H_2O$ and $Na_2B_4O_7.10H_2O$.

It should be pointed out that the present work is by no means very exhaustive, and there are several aspects of the problem which await investigation. These will be dealt with in subsequent communications. The results obtained are, however, quite sufficient to show the inadequacy of our existing knowledge relating to the Raman spectrum of crystal water, and the wealth of information which the technique of complementary filters promises to offer in this direction.

Experimental.

The spectra of the hydrated salts (Kahlbaum's chemicals) were photographed for the most part on a Hilger two-prism spectrograph ; a Fuess spectrograph of larger dispersion was employed in the case of the chlorides of magnesium and manganese. Exposures of the order of 72 hours were generally found necessary to bring out the complete details of the water-bands in the 3 μ region.

Results.

The Raman spectrum of water of crystallisation shows amazing variations in structure and intensity from substance to substance. On account

of the many subtle and intricate differences, it is very difficult indeed to give a correct and complete description of all the observed features in the case of the individual substances. These are best exemplified by the photographs reproduced in the plate. It can, however, be generally stated that water of crystallisation shows Raman frequencies between 3150 and 3650 cm.$^{-1}$ The most salient features of the water-bands observed in the individual cases are briefly reported below :—

1. $Mg(NO_3)_2.6H_2O$.—The water frequencies which are recorded strongly in the spectrum of this substance consist of four broad and diffuse lines 3250 (1*b*), 3370 (4*bd*), 3495 (3*bd*) and 3590 (5*b*). The first and the fourth of these are clearly separated from the middle two which almost merge into each other.

2. $Ca(NO_3)_2.4H_2O$.—The Raman frequencies of the water of crystallisation appear in the spectrum as a broad and diffuse band extending from 3256 to 3600 cm.$^{-1}$ Careful examination shows that the band possesses a peculiar structure, and at least three components 3256 (1*b*), 3500 (3*bd*) and 3600 (2*b*) can be distinguished.

3. $Cd(NO_3)_2.4H_2O$.—The water-band shows a structure somewhat similar to that observed in the case of $Ca(NO_3)_2.4H_2O$, with an intensity maximum at about 3470 cm.$^{-1}$

4. $Cu(NO_3)_2.3H_2O$.—We have here the interesting example of a substance in whose spectrum, the water of crystallisation manifests itself as a set of discrete and fairly sharp lines. The observed frequencies are 3150 ($\frac{1}{2}$), 3338 (2), 3503 (2) and 3570 (1).

5. $Ce(NO_3)_3.6H_2O$.—There is a faint band at 3257 cm.$^{-1}$, followed by a broad and intense one extending over about 180 wave numbers. The latter appears to consist of two incompletely resolved components at 3400 and 3512 cm.$^{-1}$ respectively.

6. $Bi(NO_3)_3.5H_2O$.—The structure of the water-band in this case is very peculiar and interesting. There is first a very broad band extending from 3170 to 3430 cm.$^{-1}$ This band is very diffuse towards the side of the exciting line, but terminates fairly sharply on the other side. It is followed by two lines 3467 (2*b*) and 3557 (3*b*).

7. $SrCl_2.6H_2O$.—The Raman spectrum of the water of crystallisation of this substance has already been reported upon by the author (1937). It is a typical substance which the author has met with in the course of his studies, whose water of crystallisation gives rise to a narrow and very intense Raman band accompanied by a number of fainter components. The observed frequencies are 3217 (1), 3284 ($\frac{1}{2}$), 3363 (2) and 3433 (10*b*). The main band

could be seen visually through the spectrograph without the least difficulty. A similar equally intense band was also observed visually in the case of $CaCl_2.6H_2O$ crystals, but repeated attempts to photograph this band were unsuccessful because, on account of the extreme instability of the hydrate at room temperature, it invariably melted in its own water of crystallisation to a homogeneous liquid within a very short time after the exposure was started.

8. *$MgCl_2.6H_2O$*.—Although one might expect to find a close similarity between the spectrum of this substance and that of $SrCl_2.6H_2O$, this is not actually the case. The following frequencies are observed in the spectrum of this substance:—1600 (0*b*), 3173 (1*b*), 3338 (10*b*), 3395 (6*b*) and 3512 (10*b*).

9. *$MnCl_2.4H_2O$*.—Two broad lines 3312 (2*b*) and 3395 (2*b*) followed by a diffuse band extending over some 100 wave numbers are found in the Raman spectrum of this substance.

10. *$CuSO_4.5H_2O$*.—Three diffuse bands 3172 (3*bd*), 3367 (2*bd*) and 3470 (1*bd*) are observed in the 3 μ region. Considering the diffuse nature of the bands, the above frequencies agree reasonably well with the values 3211, 3377 and 3497 reported by Nisi.

11. *$Na_3VO_4.12H_2O$*.—The spectral features of the water of crystallisation are somewhat peculiar in this substance. The spectrum shows a broad and intense band extending from 3150 to 3467 cm.$^{-1}$ This is followed by a strong line whose frequency shift is 3636 cm.$^{-1}$

Besides these, the spectrum shows two lines 764 (2*b*) and 812 (12*b*), which evidently originate from the vibrations of the $(VO_4)^{---}$ ion.

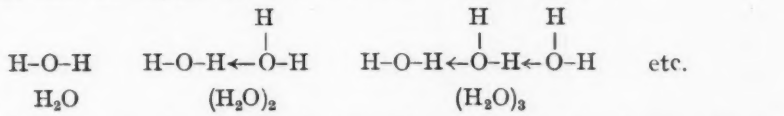
12. *$Na_3PO_4.12H_2O$*.—The structure and frequencies of the water-bands are exactly the same as in the case of $Na_3VO_4.12H_2O$. Two additional frequencies 943 (4*s*) and 993 (0) are also observed in the spectrum.

13. *$Na_2CO_3.10H_2O$*.—On account of the extreme instability of the decahydrate at room temperature, it was not possible to obtain a well-exposed picture. The spectrum obtained after an exposure of about six hours showed a broad band in the 3 μ region extending from about 3150 to 3600 wave numbers. The inactive frequency of the $(CO_3)^{--}$ ion was also recorded in the spectrum as a sharp line at 1060 cm.$^{-1}$

14. *$Na_2B_4O_7.10H_2O$*.—This is an example of a substance whose water of crystallisation gives rise to fairly sharp spectral lines well separated from one another. The following frequencies are observed:—3172 (2), 3312 (2), 3432 (4*b*), 3500 ($\frac{1}{2}$), 3535 ($\frac{1}{2}$) and 3580 (4*s*). Two additional frequencies 763 ($\frac{1}{2}d$) and 942 ($\frac{1}{2}s$), presumably due to B–O oscillations, are also recorded in the Raman spectrum of crystalline borax.

Discussion of Results.

It is not possible in the present state of our knowledge regarding the nature of crystal water to give any satisfactory explanation for the diversity and complexity of the spectral features enumerated in the preceding section. Indeed, in spite of the very numerous researches, even the Raman spectrum of liquid water has not been satisfactorily explained or understood. There is strong evidence to show that the molecules of water are highly polymerised, and it is generally supposed that this is responsible for the peculiar behaviour of water. The mechanism of polymerisation is supposed to be the formation of a "co-ordinate linkage" between the hydrogen atom of one water molecule and the oxygen atom of another. Thus we have



It is, of course, conceivable that the vibrations of these molecular complexes are extremely complicated, although we are still confronted with the fundamental question, "Are we to consider the co-ordinate and covalent linkages as identical from the standpoint of vibrational spectra?" According to Sidgwick (1927), it is *a priori* not improbable that polymerisation does take place even in the case of crystal water. Besides, it is to be remembered that the molecules of crystal water are under the influence of the very high electric fields of the electrically charged ions. We should not, therefore, be surprised at the observed complexity of the Raman spectra of crystal water. Certain lines of investigation such as the influence of temperature, effect of substitution of H_2O by D_2O, etc., on the Raman spectra of crystal water suggest themselves as possible methods of approach towards a better understanding of these spectra.

In conclusion, the author's grateful thanks are due to Professor Sir C. V. Raman, for his kind and encouraging interest in the present work.

Summary.

After a brief survey of the earlier work on the Raman spectra of inorganic nitrates, Part I of the paper gives a detailed account of the Raman spectra of the following eleven crystalline nitrates:—$NaNO_3$, KNO_3, NH_4NO_3, $Pb(NO_3)_2$, $Sr(NO_3)_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $Ca(NO_3)_2.4H_2O$, $Mg(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Ce(NO_3)_3.6H_2O$ and $Bi(NO_3)_3.5H_2O$, photographed by the technique of complementary filters. It is found that the results of earlier investigators are incomplete in the case of all the nitrates excepting $NaNO_3$. The frequencies of the $(NO_3)^-$ ion are recorded as three sharp lines 723 (2),

1069 (12) and 1385 (6), in the spectrum of crystalline $NaNO_3$. The corresponding frequencies of KNO_3 are 715 (2), 1050·5 (12), 1343 (3) and 1360 (3). The splitting of the nitrate frequency in the 1300 region in the spectrum of KNO_3 is noticed for the first time, and is ascribed to the fact that its crystal structure is different from that of $NaNO_3$. The spectra of the nitrates of bi- and tri-valent metals are characterised by extreme complexity, and a large number of frequencies are observed between 1100 and 1650 cm.$^{-1}$, many of which are broad and diffuse. The main nitrate frequency near 1050 cm.$^{-1}$ is split up into two components in the spectra of copper and cerous nitrates.

Part II of the paper deals with the Raman spectra of the water of crystallisation of the following fourteen hydrated crystals:—$Mg(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, $Ce(NO_3)_3.6H_2O$, $Bi(NO_3)_3.5H_2O$, $SrCl_2.6H_2O$, $MgCl_2.6H_2O$, $MnCl_2.4H_2O$, $CuSO_4.5H_2O$, $Na_3VO_4.12H_2O$, $Na_3PO_4.12H_2O$, $Na_2CO_3.10H_2O$ and $Na_2B_4O_7.10H_2O$. The results vary very much from substance to substance. It can generally be stated that water of crystallisation gives rise to Raman frequencies between 3150 and 3650 cm.$^{-1}$ The water frequencies observed in the crystals are sharp lines in some cases, broad and diffuse lines in others, and at times broad bands terminating in sharp lines. The intensities of the water-bands differ from one substance to another; the hydrated chlorides of calcium, strontium and magnesium show particularly intense water-bands.

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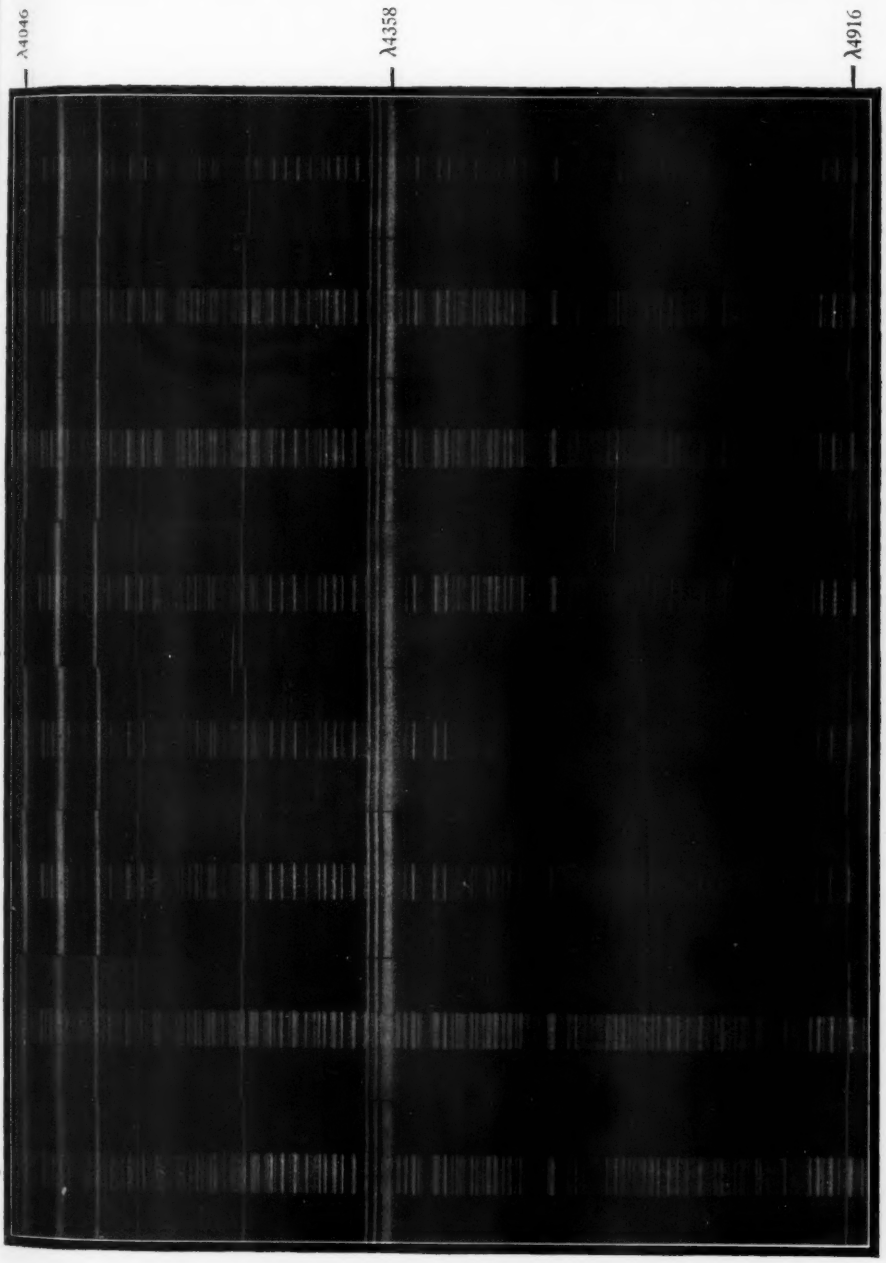

FIG. 1. Raman spectra of crystal powders.

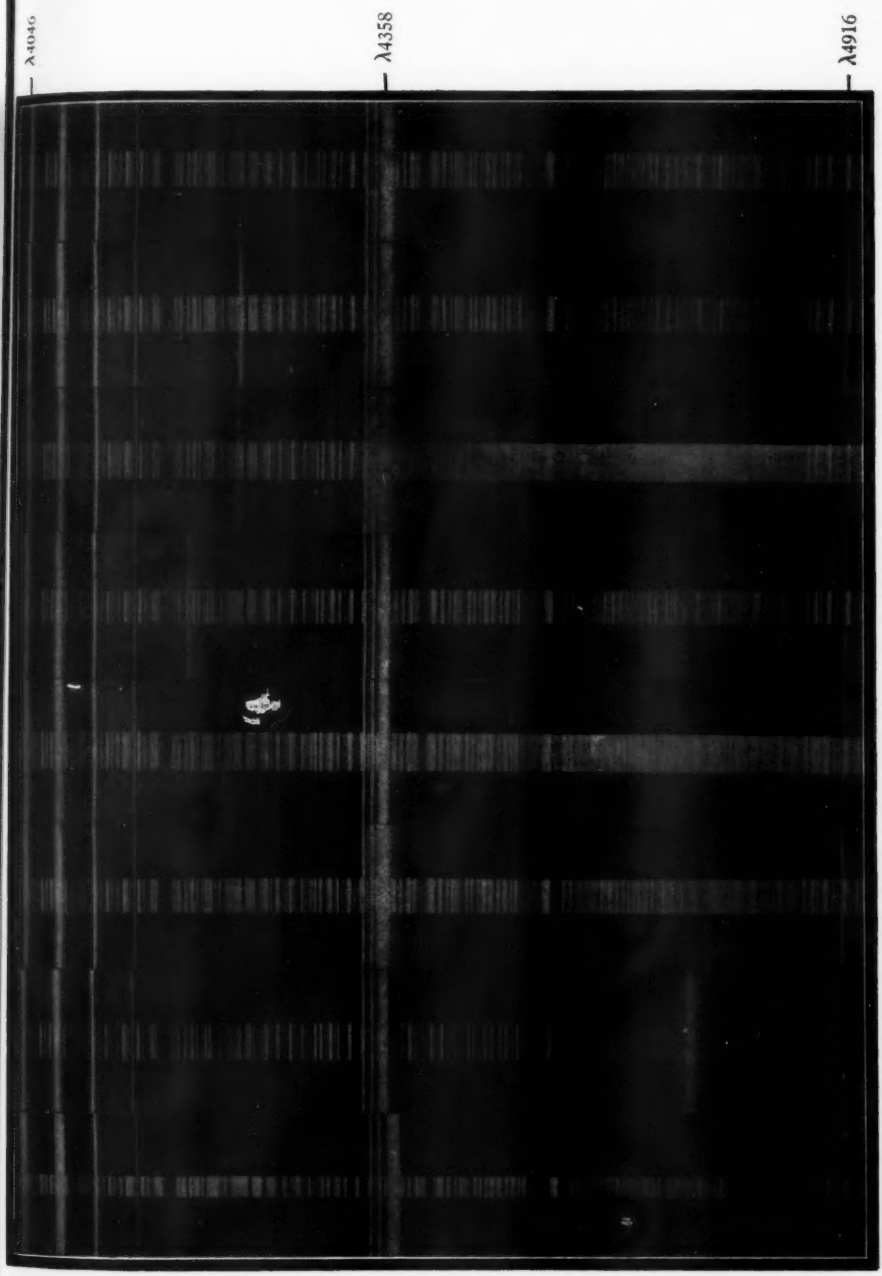

FIG. 2. Raman spectra of crystal powders.

THE ELASTIC PROPERTIES OF MOTHER-OF-PEARL.

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1. Introduction.

From the theoretical standpoint, measurements of the elastic properties of solids possess the greatest significance when they relate to the material in the form of single crystals ; the uniformity in the spacing and orientation of the units composing the crystal lattice opens up the possibility of theoretical computations of the elastic properties for comparison with the experimental results. The great majority of the solids used in the arts and industries are, however, not single crystals but aggregates having a more or less complex structure. The relation between the elastic properties of these aggregates and those of the crystalline units of which they are made up is obviously a subject of considerable importance. It may naturally be assumed that the properties of polycrystalline aggregates will depend to a considerable extent on those of the single crystals which form them. The order and arrangement of the crystallites are obviously of importance in this connection. Thus a random orientation in space of intrinsically anisotropic crystals may be expected to result in an elastically isotropic body while an orientation about a linear axis will result in a fibre structure and consequent elastic anisotropy. In many substances, these considerations are further complicated by the presence of a substance usually of the nature of a cementing material which helps to bind the various crystallites together. The nature, quantity and distribution of this cementing material will influence in a marked manner, the elastic properties of the main substance. This cementing material may, in some cases, be an amorphous phase of the same chemical nature as the crystallites or it may be an entirely foreign substance.

The latter type of cementing substance occurs in mother-of-pearl, the subject of the present investigation. Mother-of-pearl which is the nacreous layer in a large class of molluscan shells consists mainly (from 85 to 95 per cent. of its weight) of crystals of calcium carbonate, held together by an organic protein matter called conchyolin. Chalk, as is well known, occurs in nature in two distinctly crystalline varieties known as calcite and aragonite. It

is the latter form of it that occurs in mother-of-pearl. A detailed experimental study of the elastic properties of calcite and aragonite has been made by Voigt (1890, 1907). Fig. 1 gives the principal sections, according to Voigt, of the elastic surfaces of aragonite and Fig. 2 those of calcite. The

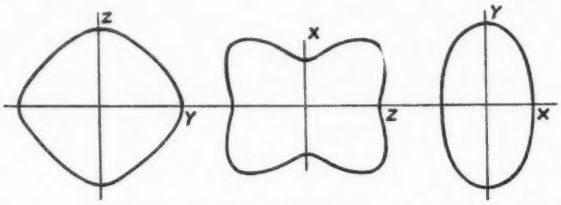

FIG. 1(*a*). Dehnungsmoduln of Aragonite (Voigt, 1907).

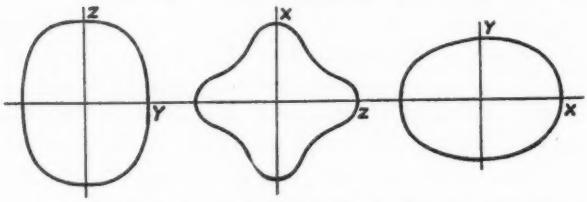

FIG. 1(*b*). Drillungsmoduln of Aragonite (Voigt, 1907).

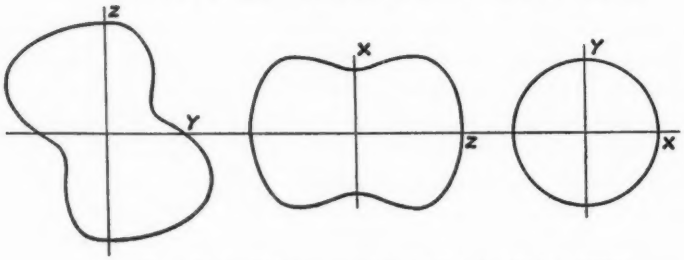

FIG. 2(*a*). Dehnungsmoduln of Calcite (Voigt, 1890).

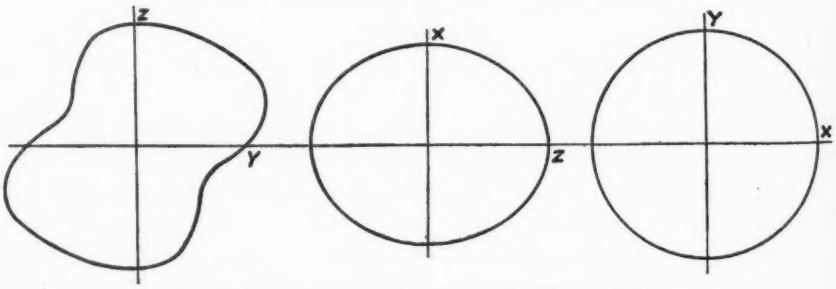

FIG. 2(*b*). Drillungsmoduln of Calcite (Voigt, 1890).

striking difference in elastic properties between the two forms is obvious from the figures. In a recent series of papers, Oke (1936) has made a theoretical computation of the elastic constants of aragonite and calcite based on Born's Lattice Theory of Crystal Structure and he finds a satisfactory agreement between his calculations and the experimental values of Voigt. According to Oke, the cause of the difference in the elastic properties between calcite and aragonite is to be traced to the difference in the relative positions of the Ca^+ and CO_3^- ions in the two crystals. The elastic anisotropy is more marked in the case of aragonite than in calcite. Indeed in the xy-plane, while calcite is isotropic, the Young's modulus of aragonite along the x-axis is quite double that along the y-axis. As we shall see later, this feature makes itself felt in the elastic properties of mother-of-pearl.

2. Structure of Mother-of-pearl.

Dating from the time of Brewster (1853), the structure of mother-of-pearl has formed the subject of numerous investigations, amongst which those of Schmidt (1924) should be specially mentioned. As is well-known mother-of-pearl has got a laminated structure, consisting of alternate layers of aragonite and conchyolin. Each aragonite layer is in turn made up of a number of platelets of aragonite crystals, the platelets being bound to one another by intervening conchyolin. According to Schmidt, the aragonite crystallites forming the platelets in all the shells, all lie with their c-axes normal to the plane of the platelets, which in turn lie parallel to the surface of the shell. Schmidt had also realised that the thickness of the protein layer intervening between the aragonite layers was small, in comparison with the thickness of the latter, a conclusion also arrived at by Raman (1935) by a study of the laminar diffraction of light by the surface of these shells. By a study of the body colours and diffusion haloes exhibited by these shells, Raman has further established that the platelets of aragonite forming the layers in any shell are sensibly of uniform dimensions and spaced therein in a regular manner. The three great groups of molluscs, *viz.*, the Bivalves, the Gastropods and the Cephalopods are sharply differentiated by striking differences in their diffusion haloes which further indicate that the arrangements of the crystalline particles in nacre are very difficult in the groups. He thus finds that in the Bivalves, there is a more or less regular orientation of the aragonite crystals with respect to the lines of growth in the plane of the shell, a random orientation in the Gastropods and an intermediate orientation in the Cephelopods. From the angular size and general character of the diffusion haloes Raman has been able to estimate the size and disposition of the crystalline particles. An X-ray investigation of the nacre of various shells has enabled Ramaswami

(1935) to confirm the inferences drawn from these optical observations and to establish definitely the orientation of the crystals in the different shells. He finds that in all the shells examined the *c*-axis is normal to the shell surface while the *a*- and *b*-axes lying in the plane of the shell have got a regular orientation (with only an error of about 5°) with respect to the lines of growth in the Lamellibranchs and a quite random orientation in the Gastropods. In *Nautilus Pompilius* a preferred orientation is complicated with twinning and a large error of orientation of about 15°. Ramaswami's observations on *Nautilus* are of special interest from the viewpoint of the present investigation and are referred to in detail later on. Differences between the diffusion haloes of shells within the same group observed by Raman are correlated with variations in the size of the platelets of aragonite and a varying amount of error in their orientation. By observations with parallel and convergent polarised light under the petrographic microscope, Rajagopalan (1936) has made measurements on the size and arrangement of the crystal particles in the various shells and finds confirmation of the previous observations. In the present investigation, the elastic properties of nacre of different shells have been studied and it is shown that the relation between the elastic properties of aragonite and the shells is intelligible in view of the structural details established by previous investigators. As is shown later, it has also been possible to obtain a quantitative estimate of the protein distribution in nacre.

3. *Preparation of the Specimens.*

In Sir C. V. Raman's private collection of shells, large and well-formed shells were available belonging to the various families and the following table gives details of the shells that were employed in the present investigation.

TABLE I.

Description of the shells studied.

No.	Family	Name of shell	Source	Approximate dimensions
1	Lamellibranchs	*M. Margaratifera*	Bombay Market	8″ × 6″
2	,,	*M. Vulgaris*	Rameswaram (Madras)	$2\frac{1}{2}$″ × $1\frac{3}{4}$″
3	Gastropods	*Turbo*	Bombay Market	6″ diameter, 5″ height
4	,,	*Trochus*	Andamans	5″ diameter, 4″ height
5	,,	*Heliotis* (Abalone C.)	California	8″ × 5″
6	Cephalopods	*Nautilus Pompilius*	Ennur (Madras)	6″ diameter, 3″ height

As will be seen from the above table except *M. Vulgaris* of which a specimen larger than about 2″ was not available, all the other shells were quite large specimens and it was not a difficult matter to prepare a few good test pieces for measuring the elastic constants. Fig. 3 represents the general appearance of a specimen of *M. Margaratifera* after the outer prismatic layer has been cleaned up by a rapid application of dilute hydrochloric acid.

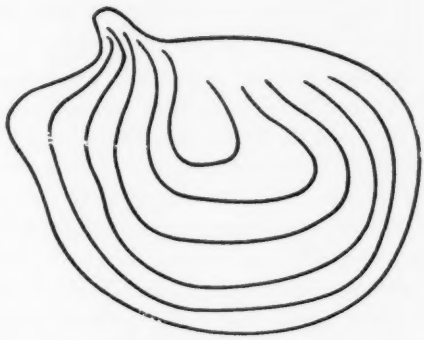

FIG. 3. Lines of Growth in *M. Margaratifera.*

The lines of growth are clearly discernible as large curved lines running nearly parallel to one another and it is easy to choose a place where the lines are sensibly straight over distances of 3 or 4 cm. and in such places a strip of about 5 mm. width and as great a length as possible is marked out with its length inclined at a known definite angle to the lines of growth. The strip is afterwards carefully cut out with a jeweller's saw and ground on a thick glass sheet with emery powder of increasing fineness so as to remove the outer prismatic layer completely and polish the nacreous layer sufficiently smooth. The characteristic iridescent reflection helps to ensure during the grinding that the surface of the specimen is parallel to the lamination planes. Thus out of the strip cut out, a specimen of about 3 cm. length, 5 mm. width and 1 mm. thickness is carefully prepared. The final grinding is done with the finest grade emery powder and the dimensions are checked at different places with a screw gauge or vernier calipers to within half a per cent. deviation from the mean.

For getting transverse sections a specially thick large shell of *M. Margaratifera* whose mean thickness was about 5 mm. was chosen and at its thickest portion, a strip normal to the shell surface was cut off in a direction parallel to the lines of growth. The laminations are clearly discernible as lines

running parallel to the surface of the shell. This strip is first ground so as to have a thickness of about 2 mm., *i.e.*, in the direction perpendicular to the lines of growth in the plane of the shell. In favourable positions the thickness of the shell was as much as 7 or 8 mm. A specimen with its length along or at a definite known inclination to the *c*-axis is cut out and carefully polished. The width of the specimen was along the direction of the lines of growth and had a magnitude of about 3 or 4 mm. The thickness in the plane of the shell at right angles to the lines of growth was of the order of a mm. or less in the finished specimen.

In the case of *Nautilus*, though large shells were chosen for the experiment, on account of the very large curvature and the small thickness of the shell, specimens of only about 15–20 mm. length could be prepared. Further, since it was found that the Young's modulus showed sudden changes from direction to direction, it was considered worthwhile checking up the values obtained with one shell by experiments conducted with specimens obtained from an independent shell and it will be seen from tables when the results for both the shells are given that within the limits of experimental errors the results are comparable. In *Trochus* a difficulty was experienced in getting the final surface of the test-piece parallel to the lamination planes. This shell has got a steep spiral structure and there is a large skew angle between the surface of the shell and the laminations. Further the iridescence of this shell is not quite marked which adds to the difficulty of getting a properly ground specimen. Though great care was of course taken in the preparation of the specimens, it is doubtful in the case of *Trochus* whether reasonable success was achieved in making the surface parallel to the laminations.

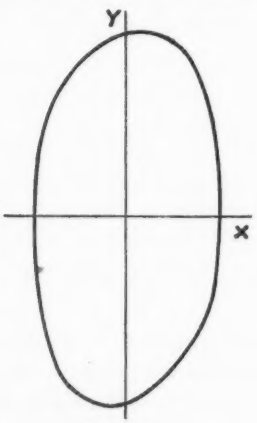

FIG. 4.

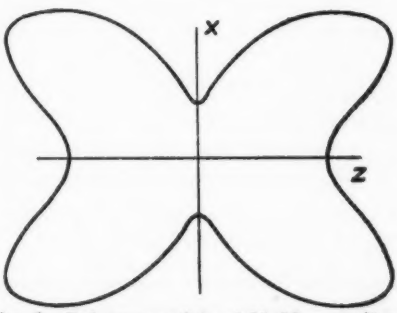

FIG. 5. Dehnungsmoduln of *M. Margaratifera*.

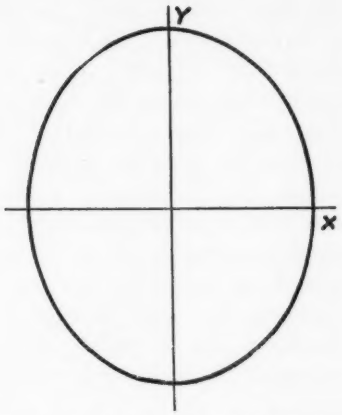

FIG. 6. Drillungsmoduln of *M. Margaratifera.*

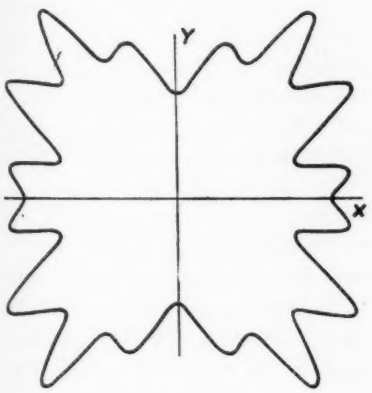

FIG. 7.
Young's modulus of *Nautilus Pompilius.*

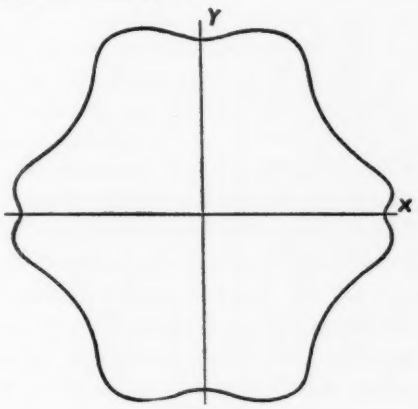

FIG. 8.
Young's modulus of a Twinned Crystal.

4. Experimental Arrangement.

(*i*) *Young's Modulus.*—(*a*) For determining the Young's modulus of specimens of at least 2 cm. length, Köenig's method of bending was adopted. Two adjustable robust knife-edges were bolted on to a heavy lathe-bed and the specimen was supported on the two knife-edges. Two small plane mirrors were fixed on to the upper surface of the specimen with their planes as nearly perpendicular to the specimen surface as possible and their reflecting surfaces facing each other. At a distance of about a metre from one of the mirrors was supported a vertical mm. scale which was strongly

illuminated with an electric lamp close at hand. On the side of the apparatus remote from the scale was mounted a telescope for viewing the image of the scale as reflected by the two mirrors. A stirrup carried on a third light and small knife-edge, resting across the specimen exactly midway between the two supporting knife-edges carried a light scalepan. Care was taken to see that the two mirrors were arranged symmetrically with respect to the two knife-edges and the distance apart between them was equal to or slightly greater than that between the two knife-edges. For the same shell the experiment was repeated with different distances between the knife-edges and with samples of different thickness. The results justified the anticipation that within limits, the elastic modulus would be independent of the dimensions of the specimen. In calculating the value of the modulus from the observed displacement in the reading of the telescope, the following formula was employed :

$$q = \frac{3Wl^2(2D + r)}{2bd^3x} \text{ where}$$

q is the Young's modulus of the material,
W is the weight applied at the midpoint,
D is the distance between the scale and the mirror facing it,
r is the distance between the two mirrors,
l is the distance between the two knife-edges,
b is the width of the specimen,
d is the thickness of the specimen, and
x is the observed displacement of the scale reading.

(*b*) For determining the Young's modulus of specimens of 1 cm. length or thereabouts, a single cantiliver method of bending was employed. The specimen was firmly clamped horizontally at one end to a stiff short vertical pillar bolted on to the lathe-bed and was loaded by means of a scale-pan suspended from a stirrup resting on the specimen near its free end. A thin strip of plane mirror attached vertically to the free end of the specimen and a telescope and scale mounted at about a metre in front were employed to observe the deflection of the specimen. The modulus was calculated by the formula,

$$q = \frac{12Wl^3D}{bd^3x},$$

where l represents the distance on the specimen between the clamped end and the stirrup carrying the scalepan and the other symbols signify as in the previous formula.

A test experiment conducted on the same specimen by methods (*a*) and (*b*) showed that the results obtained were comparable.

(*ii*) ***Rigidity Modulus.***—For determining the rigidity modulus the following arrangement was found convenient. A stout vertical metallic pillar about 20 × 2 × 2 cm. was bolted rigidly to the lathe-bed and carried two cross-arms. The lower cross-arm was a fixed one while the upper one was capable of being clamped anywhere along the pillar. The specimen was, at its upper extremity, firmly clamped to the upper arm and at its lower extremity was clamped axially to a disc. A stout, short, smooth pin attached axially to the lower face of the disc was passed just freely through a hole in the lower arm vertically below the upper clamp and served to prevent lateral oscillations of the specimen while, however, allowing free rotation. A piece of fine silk thread was doubled round a pin fixed on the rim of the disc and its two extremities left the disc tangentially at opposite ends of a diameter and passing over two smooth ball-bearing pulleys, carried light scalepans at the ends. Two small plane mirrors carried on very narrow metallic strips were fixed at a suitable distance apart on the specimen and a telescope and a scale were arranged at a distance of about a metre in front of the mirrors. Since the vertical distance between the two mirrors was of the order of 2 cm. or less, it was possible to get the images of the scale as reflected by the two mirrors simultaneously in focus in the field of view of the telescope. When equal weights were added to the two scalepans, the lower end of the specimen was rotated relative to the upper end and the twist varying as the distance from the clamped end produced different angles of rotation of the two mirrors and corresponding different changes in the telescope reading. The readings of the telescope thus helped to get the relative angle of twist between the two sections and the rigidity modulus, n, was calculated by means of the formula,

$$n = \frac{32\,Mgdlx}{ab^3\left(\frac{16}{3} - 3{\cdot}361\,\frac{b}{a}\right)(x_1 - x_2)}, \text{ where}$$

M represents the mass at each end of the string,
g is the acceleration due to gravity,
d is the diameter of the disc D,
l is the distance between the two mirrors,
x is the distance between the scale and the mirrors,
a is the width of the specimen,
b is the thickness of the specimen, and
x_1 and x_2 are the observed displacements of the readings from the two mirrors.

This formula is applicable only to specimens whose width is at least six times its thickness and care was taken to see that all the specimens

employed satisfied this condition. Further since specimens less than 2 cm. in length could not be satisfactorily used in the apparatus, the rigidity modulus in such cases has not been determined.

5. *Results.*

The following tables give the results of the experiments on the various shells. The results are also represented graphically on polar co-ordinates so that the radius vector in any direction gives the modulus along that direction, the x-axis being chosen to represent the direction of the lines of growth. For purposes of comparison with Voigt's curves, the values of Dehnungsmodul and Drillungsmodul are plotted instead of Young's modulus and rigidity modulus. The reciprocal of the Young's modulus in gm. per square mm. is the Dehnungsmodul and the reciprocal of the rigidity modulus also in gm. per square mm. is the Drillungsmodul.

TABLE II.

Young's modulus of M. Margaratifera *in the plane of the shell.*

No.	Inclination to lines of growth	Young's modulus in dynes/cm.^{2}	Dehnungswiderstand	Dehnungsmoduln
1	0°	$9{\cdot}25 \times 10^{11}$	$9{\cdot}46 \times 10^{6}$	$1{\cdot}06 \times 10^{-7}$
2	15°	7·82	8·00	1·25
3	30°	7·38	7·55	1·33
4	45°	8·06	8·24	1·21
5	60°	7·01	7·16	1·40
6	75°	6·06	6·20	1·61
7	90°	5·74	5·87	1·70
8	105°	6·64	6·79	1·47
9	120°	7·23	7·39	1·35
10	135°	7·37	7·54	1·32
11	150°	7·59	7·76	1·29
12	165°	9·66	9·88	1·01

TABLE III.

Young's modulus of M. Margaratifera *in the transverse section.*

No.	Inclination to the c-axis	Young's modulus in dynes/cm.^{2}	Dehnungswiderstand	Dehnungsmoduln
1	0°	$2{\cdot}12 \times 10^{11}$	$2{\cdot}17 \times 10^{6}$	$4{\cdot}61 \times 10^{-7}$
2	30°	1·29	1·32	7·59
3	45°	1·25	1·28	7·80
4	60°	2·81	2·87	3·48
5	75°	3·23	3·30	3·03

TABLE IV.

Rigidity modulus of M. Margaratifera *in the plane of the shell.*

No.	Inclination to lines of growth	Rigidity modulus in dynes/cm.^{2}	Drillingswiderstand in gm./cm.^{2}	Drillingsmoduln
1	0°	$2{\cdot}66 \times 10^{11}$	$2{\cdot}72 \times 10^{7}$	$3{\cdot}68 \times 10^{-7}$
2	15°	2·62	2·68	3·73
3	30°	2·52	2·58	3·88
4	45°	2·25	2·30	4·35
5	60°	2·39	2·44	4·09
6	75°	2·10	2·15	4·66
7	90°	2·14	2·19	4·57
8	105°	2·16	2·21	4·53
9	120°	2·42	2·47	4·04
10	135°	2·36	2·41	4·15
11	150°	2·40	2·45	4·08
12	165°	2·73	2·81	3·58

TABLE V.

Elastic moduli of Turbo *in the plane of the shell.*

No.	Inclination to lines of growth	Young's modulus in dynes/cm.^{2}	Dehnungs-moduln	Rigidity modulus in dynes/cm.^{2}	Drillungs-moduln
1	0°	$6{\cdot}84\times10^{11}$	$1{\cdot}43\times10^{-7}$	$2{\cdot}35\times10^{11}$	$4{\cdot}16\times10^{-7}$
2	30°	6·84	$1{\cdot}43\times10^{-7}$	2·41	4·06
3	60°	6·89	1·42	2·36	4·15
4	90°	6·43	1·52	2·48	3·94
5	120°	6·68	1·46	2·40	4·08
6	150°	6·79	1·44	2·38	4·11

TABLE VI.

Young's modulus of Nautilus Pompilius *in the plane of the shell.*

No.	Inclination to lines of growth	Young's modulus in dynes/cm.^{2}		
		1st Shell	2nd Shell	Average
1	0°	$4{\cdot}32\times10^{11}$	$4{\cdot}44\times10^{11}$	$4{\cdot}38\times10^{11}$
2	7·5°	3·26	3·41	3·34
3	15·0°	2·31	2·23	2·27
4	22·5°	2·78	2·90	2·84
5	30·0°	3·81	3·86	3·84
6	37·5°	3·72	3·86	3·79
7	45·0°	2·98	3·09	3·04
8	52·5°	4·47	4·61	4·54
9	60·0°	2·86	2·77	2·82
10	67·5°	3·02	3·13	3·08
11	75·0°	3·10	3·00	3·05
12	82·5°	2·41	..	2·41
13	90·0°	1·88	1·98	1·93

TABLE VII.

Young's modulus of other shells in the plane of the shell.

No.	Shell	Young's modulus above lines of growth	Young's modulus across lines of growth
1	*M. Vulgaris*	$4 \cdot 26 \times 10^{11}$ dynes/cm.^{2}	....
2	*Trochus*	$3 \cdot 37 \times 10^{11}$,,	$3 \cdot 31 \times 10^{11}$ dynes/cm.^{2}
3	*Heliotis* (Abalone)	$4 \cdot 36 \times 10^{11}$,,	$3 \cdot 27 \times 10^{11}$,,

Note.—The Young's modulus normal to the lines of growth has not been determined in the case of M. Vulgaris since the shell was a small thin one with a large curvature.

6. *Relation between Structure and Elasticity.*

An analysis of the results given in the previous section brings out prominently some interesting facts and an attempt is made to correlate those facts with the known structural details, reserving a detailed consideration of individual shells to a later stage.

It will be noticed that the elastic properties show a more or less regular variation with direction in the case of shells of the Lamillibranchs wherein we know from independent evidence there is a definite orientation of the crystals, while in the Gastropods where there is random orientation in the plane of the shell, the directional variation of elasticity is irregular and within the limits of experimental errors and structural faults. (In *Heliotis* C., however, there is evidence of a definite though small elastic anisotropy, a fact agreeing with Ramaswami's observation that in this shell there is an arrangement similar to that in *M. Vulgaris* but with a large error of orientation varying from 60 to 90°.) In *Nautilus* where an intermediate behaviour will be expected, a totally peculiar variation is observed and it will be considered later on. Again with in the same zoological group it is observed that the elasticity varies considerably from shell to shell. Thus the Young's modulus of *M. Margaratifera* along the lines of growth is 9·3 while the corres ponding value for *M. Vulgaris* is 4.3. Among the Gastropods, *Turbo* possesses a value of 6.5 for its Young's modulus while it is about 3·3 and 4·3 for *Trochus* and *Heliotis* C., respectively. The absolute magnitude of the elastic modulus of any shell is also of interest. Thus in *M. Margaratifera* where the orientation is of a high order of regularity, the Young's modulus in any direction is considerably less than that of aragonite in a corresponding direction. The average value of Young's modulus for a random distribution of aragonite will be about 9·3 while the actual value for *Turbo* in which a completely random orientation is known to exist is in the whereabouts of 6·5.

That the elastic anisotropy of the shells should depend upon the degree of orientation of the aragonite crystals in the plane of the shell is a necessary consequence of the fact that the aragonite crystal itself possesses marked elastic anisotropy. Hence an orderly disposition of the crystals will more or less tend to preserve the anisotropy, while a quite random orientation will average out the differences to a mean value. Comparing Figs. 1(*a*) and 7, we see that the elastic curves of aragonite in the *xy*-plane and of the shell *M. Margaratifera* in the plane of the shell are quite similar (except for the ratio of the axes) and that the maximum value of the Young's modulus of aragonite occurs along its *a*-axis and of the shell nearly along the lines of growth. From this we infer that in *M. Margaratifera* the aragonite crystals are oriented in the plane of the shell with their *a*-axis, more or less, along the lines of growth.

Still the fact that the actual elasticity is considerably less than the probable value for the distribution concerned calls for an explanation. We know that in all these shells, though the bulk of the matter consists of aragonite crystals, the crystal particles themselves are bound together in a framework of conchyolin. It is also known that conchyolin possesses a very low elasticity of the order of $0{\cdot}3\times10^{11}$ dynes/cm.^{2} and that the resulting elasticity of a mixture of two substances will have an intermediate value. The drop in the elasticity of the shells is therefore to be attributed to the effect of the binding material. This assumption gets further support from the fact that within the same family, the drop in elasticity increases with the conchyolin content of the shells, as is seen from the following table.

TABLE VIII.

Relation between Young's modulus and Conchyolin content.

No.	Family	Shell	Percentage by weight of conchyolin	Young's modulus along lines of growth
1	Lamellibranchs	*M. Margaratifera*	4·2 — 5·0	$9{\cdot}3\times10^{11}$ dynes/cm.^{2}
2	,,	*M. Vulgaris*	10·0 — 11·0	4·3 ,,
3	Gastropods	*Trochus**	2·5 — 3·0	3·4 ,,
4	,,	*Turbo*	6·5 — 7·5	6·5 ,,
5	,,	*Heliotis* (Abalone C.)	8·0 — 9·0	4·3 ,,
6	Cephalopods	*Nautilus Pompilius*	14·0 — 15·0	4·5 ,,

* [*Trochus* appears to be an exception but may not be really so. The low value of the Young's modulus in spite of low conchyolin content might be due to want of parallelism between the surface of the test-piece and the plane of laminations, a difficulty that has already been referred to. As seen from Table IV, even a small inclination to the lamination plane brings the Young's modulus down from a value 9·3 in the plane of the shell to 3·3 for an inclination of only 15° therefrom.]

7. *M. Margaratifera.*

By making use of the observed values of the Young's modulus along and across the lines of growth in the plane of the shells, in combination with the microscopic data on the size of the crystalline units, it is possible to calculate the distribution of conchyolin in the structure. Considering the nature of the quantities involved in the calculation and the unavoidable approximations introduced therein, the results are at best only near the truth but their great claim to consideration lies in the fact that the value of the Young's modulus perpendicular to the plane of the shell deduced from the results of the calculation agrees remarkably well with the experimental value. Indeed, it was the startlingly low value of the Young's modulus in this direction according to the calculations that was the incentive for the rather difficult experimental determination of this quantity and it is gratifying to note that the trouble proved to be worth taking.

A detailed calculation is given for the shell *M. Margaratifera* since only in this case all the necessary optical and other data were available. The architecture of this shell can be compared to a brickwork on a microscopic scale wherein the particles of aragonite form the bricks and the conchyolin forms the mortar. Assuming the platelets of aragonite to be approximately rectangular, let its dimensions be α, β and γ along the crystallographic axes a, b and c and let us choose the axes of co-ordinates, x, y and z respectively parallel to a, b and c. If we assume that the conchyolin surrounding the platelet all round has got a thickness $\partial\alpha$ along a, $\partial\beta$ along b and $\partial\gamma$ along c, the unit of structure can be taken as platelet of aragonite with the adjoining conchyolin layers on one set of three mutually perpendicular faces. In effect the structural unit becomes a brick of dimension $(\alpha + \partial\alpha)$, $(\beta + \partial\beta)$, and $(\gamma + \partial\gamma)$, the $\alpha\beta\gamma$-portion of which consists of aragonite and the $\partial\alpha$, $\partial\beta$ $\partial\gamma$ portion consists of conchyolin. Since the entire shell consists of a packing of these structural units, the Young's modulus of the shell in any direction will be the same as that of the structural unit in that direction. Hence we shall now proceed to deduce a general expression for the Young's modulus of the structural unit in any direction.

Let q_a, q_b and q_c be the Young's modulus of aragonite along the a, b and c axes respectively and let q be the Young's modulus of conchyolin assumed isotropic and let q_x, q_y and q_z be the required values of the Young's modulus of the structural unit along the x, y and z-axes respectively.

In order to find the total effect in any direction of all the conchyolin layers, we shall consider the effect first of the layer normal to that direction and then of the layers parallel to that direction. Thus in order to find the

Young's modulus q_x, we shall first consider the effect of the layer of thickness $\partial\alpha$ on the aragonite and then the effect of the layers $\partial\beta$ and $\partial\gamma$. If a stress of magnitude S acts on the structural unit parallel to the x-axis,

Strain along the x-axis of the aragonite portion $= \frac{S}{q_a}$

and strain ,, ,, conchyolin ,, $= \frac{S}{q}$

The corresponding extensions are $\frac{S}{q_a}\,\alpha$ and $\frac{S}{q}\cdot\partial\alpha$ respectively.

$$\text{Total strain } \epsilon = \frac{\frac{S}{q_a}\alpha + \frac{S}{q}\partial\alpha}{(\alpha + \delta\alpha)}$$

$$\therefore \text{ Modulus } q' = \frac{S}{\epsilon} = \frac{\alpha + \partial\alpha}{\frac{\alpha}{q_a} + \frac{\partial\alpha}{q}} = \frac{q_a q\,(\alpha + \partial\alpha)}{q\alpha + q_a\,\partial\alpha} \qquad (1)$$

Next to find the effect of $\partial\beta$ and $\partial\gamma$ on q', consider a section of the structural unit normal to the x-axis. The thickness of the conchyolin layer in the ab-plane is $\partial\gamma$ and that in the ac-plane is $\partial\beta$. Let us consider a uniform linear strain, e, along the x-axis.

Force on the aragonite face along the x-axis $= eq'\beta\gamma$.

Force along the x-axis on the conchyolin layer of thickness $\partial\gamma = eq\,(\beta + \delta\beta)\,\delta\gamma$

Force ,, ,, thickness $\partial\beta = eq\gamma\cdot\partial\beta$.

Total force along the x-axis $= (q'\beta\gamma + q\beta\partial\gamma + q\gamma\partial\beta)e$.

(In this expression and in the sequel, products of $\partial\alpha$, $\partial\beta$ and $\partial\gamma$ among themselves are neglected as quantities of the second and third order of magnitudes.)

$$\text{Final modulus along the } x\text{-axis} = q_x = \frac{(q'\beta\gamma + q\beta\partial\gamma + q\gamma\partial\beta)e}{(\beta\gamma + \beta\partial\gamma + \gamma\partial\beta)e} \qquad (2)$$

Substituting for q' in 2 from equation 1,

$$q_x = \frac{\frac{\beta\gamma\cdot q_a q(\alpha + \partial\alpha)}{q\alpha + q_a\partial\alpha} + q\beta\cdot\partial\gamma + q\gamma\cdot\partial\beta}{\beta\gamma + \beta\partial\gamma + \gamma\partial\beta}$$

$$= \frac{q\,(\alpha\beta\gamma.q_a + \beta\gamma.\partial\alpha.q_a + \alpha\beta.\partial\gamma.q + \gamma\alpha.\partial\beta.q)}{q\,(\alpha\beta\gamma + \alpha\beta.\partial\gamma + \gamma\alpha.\partial\beta) + b\gamma.\partial\alpha.q_a} \qquad (3)$$

By a cyclic variation of α, β and γ, we obtain

$$q_y = \frac{q(\alpha\beta\gamma.q_b + \gamma\alpha.\partial\beta.q_b + \beta\gamma.\partial\alpha.q + \alpha\beta.\partial\gamma.q)}{q(\alpha\beta\gamma + \beta\gamma.\partial\alpha + \alpha\beta.\partial\gamma) + \gamma\alpha.\partial\beta.q_b} \qquad (4)$$

$$q_z = \frac{q(\alpha\beta\gamma.q_c + \alpha\beta.\partial\gamma.q_c + \gamma\alpha.\partial\beta.q + \beta\gamma\,\partial\alpha.q)}{q(\alpha\beta\gamma + \gamma\alpha.\partial\beta. + \beta\gamma\partial\alpha) + \alpha\beta.\partial\gamma.q_c} \qquad (5)$$

Now of the three quantities q_x, q_y and q_z given by equations 3, 4 and 5, q_x and q_y have been determined experimentally and hence to solve for $\partial\alpha$, $\partial\beta$ and $\partial\gamma$ another equation connecting them with known quantities is necessary and this is obtained from consideration of the percentage composition of the shells. Considering the structural unit of dimensions $(\alpha+\partial\alpha)$, $(\beta+\partial\beta)$ and $(\gamma+\partial\gamma)$,

Volume of aragonite $= \alpha\beta\gamma$.

and Volume of conchyolin $= (\beta\gamma.\partial\alpha = \gamma\alpha.\partial\beta = \alpha\beta.\partial\gamma)$

We know from the chemical analysis of *M. Margaratifera* that it contains 95 per cent. by weight of aragonite and 5 per cent. by weight of conchyolin.

Hence in 100 gm. of the shell.

Weight of aragonite = 95 gm. and weight of conchyolin = 5 gm.

Density of aragonite = 2·92 gm./c.c. and of conchyolin = 1·25 gm./c.c.[2]

Hence in 100 gm. of the shell,

Volume of aragonite = 32·5 c.c. and of conchyolin = 4·0 c.c.

$\therefore$ Ratio by volume of aragonite to conchyolin $= \dfrac{32\cdot5}{4\cdot0}$

But from the dimensions of the structural unit, the ratio of the volumes

$$= \frac{\alpha\beta\gamma}{(\beta\gamma.\partial\alpha + \gamma\alpha.\partial\beta + \alpha\beta.\partial\gamma)}$$

$$\therefore \quad \frac{\alpha\beta\gamma}{(\beta\gamma.\partial\alpha + \gamma\alpha.\partial\beta + \alpha\beta.\partial\gamma)} = \frac{32\cdot5}{4\cdot0} \qquad (6)$$

From a careful study of very thin sections of the shell, under the microscope, the platelets are found to have dimensions very nearly in the ratio of 3 : 10 : 1 along the *a*, *b* and *c*-axes respectively. Hence, in our equations we can substitute for α, β, and γ the quantities 3, 10 and 1 respectively on some arbitrary unit. To get an idea of this arbitrary unit it might be remarked that the largest dimension of these platelets varies between 3 and 4 μ and hence 10 of these arbitrary units make up 3 or 4 μ.

Solving equations 3, 4 and 6 for $\partial\alpha$, $\partial\beta$ and $\partial\gamma$, we obtain

$$\partial\alpha = 0.0267$$

$$\partial\beta = 0.095$$

$$\text{and} \quad \partial\gamma = 0.1066$$

We thus find that the thickness $\partial\gamma$ of the organic material in between successive layers of aragonite is only about one-tenth the thickness of the

aragonite layer itself, a fact which confirms the views of Schmidt and Raman. Further, compared to the thickness of aragonite in corresponding directions, there is maximum protein ratio in the z-axis direction.

By substituting for $\partial\alpha$, $\partial\beta$ and $\partial\gamma$ in equation 5, the Young's modulus of the shell perpendicular to its surface comes out to be $2{\cdot}28 \times 10^{11}$ dynes/cm.^{2} The experimental value (refer Table III) is $2{\cdot}1 \times 10^{11}$ dynes/cm.^{2} and the agreement is seen to be quite good.

8. *Nautilus Pompilius.*

As mentioned previously the elastic behaviour of this shell is peculiarly interesting. This shell belongs to the Cephalopod family where the crystals of aragonite are having an intermediate degree of orientation. Hence one would have expected the elastic curve to have a shape neither so elliptic as *M. Margaratifera* nor so circular as *Turbo*. The actual curve, however, has got a very irregular shape with sudden variations between maxima and minima. If, in the calculation given in the previous section for the Young's modulus of *M. Margaratifera*, we substitute 14 per cent. of conchyolin as it exists in *Nautilus* instead of the 5 per cent. as in *M. Margaratifera*, we obtain the value of Young's modulus somewhere about $4{\cdot}8$ and it is interesting to note that in the experiment on *Nautilus*, the value of the modulus in any direction does not exceed this limit.

From X-ray studies, Ramaswami has pointed out that in *Nautilus* the crystals of aragonite are twinned across the plane 110. A group consisting of two pairs of oppositely directed twins is necessary to explain the X-ray pattern. From the point of view of elasticity, however, the two pairs are identical since the elastic curve of aragonite is symmetrical with respect to the axes. Assuming for a moment that a similar twinning were to take place in *M. Margaratifera* we can easily calculate the effect on the elastic curve of this twinning. For finding the Young's modulus in any direction of a twinned structure, we shall have to compound in that direction the effect of the two crystals inclined to each other at an angle of 120°. If q_1 and q_2 represent the Young's modulus along any direction due to the two components of a twinned structure, the resultant value q in that direction will be $\frac{2q_1q_2}{q_1 + q_2}$.

The following table gives the calculated values of the Young's modulus for a twinned structure.

TABLE IX.

Young's modulus of a twinned Structure.

No.	Inclination to lines of growth	q_1	q_2	q
1	0°	7·38	7·38	7·38
2	15°	8·06	7·82	7·94
3	30°	7·01	9·25	7·92
4	45°	6·06	7·82	6·83
5	60°	5·74	7·38	6·46
6	75°	6·64	8·06	7·28
7	90°	7·23	7·01	7·12

We see from the curve that the effect of twinning is to considerably modify the elastic behaviour. While the elastic curve of untwinned crystals in *M. Margaratifera* is a uniform ellipse, that of a twinned structure shows maxima and minima within the same quadrant. It should however be admitted that the maxima and minima of the twinned structure are fewer and much less pronounced than those representing the actual behaviour of *Nautilus*. Twinning may be responsible to some extent for the peculiar behaviour of *Nautilus* but it looks as though it is not the whole cause. The large quantity of conchyolin present in this shell, introduces, perhaps, complications in the elastic properties. One remarkable feature that was noticed in the present investigation was that, of all the shells examined, it was only *Nautilus* that showed an elastic hysteresis to a well-defined and large extent. Possibly the distribution of conchyolin in the plane of the shell is of such a character as to give rise to the sudden variations in elastic properties from direction to direction. When thin sections of this shell are examined between crossed nicols under the polarising microscope, the conchyolin appears as dark patches and the size and distribution of these dark patches are found to be of a complex character, a fact which lends further support to this idea.

9. *Summary and Conclusion.*

The elastic properties of mother-of-pearl obtained from a number of molluscan shells have been determined in different directions with respect to the lines of growth. In the case of *M. Margaratifera* the Young's modulus in the transverse section also has been determined. As a general rule it is found that in all the shells examined, the Young's modulus in any given direction diminishes with increasing protein content.

In *M. Margaratifera* there is a large elastic anisotropy in the plane of the shell, the values of the Young's modulus parallel and normal to the lines of growth being $9{\cdot}3 \times 10^{11}$ dynes/cm.^{2} and $5{\cdot}8 \times 10^{11}$ dynes/cm.^{2}, the shape of the elastic curve being similar to that of aragonite in the xy-plane. The torsional properties in the plane of the shell show also an anisotropy similar to aragonite in the xy-plane. These observations agree well with the known existence of orientation in the plane of the shell of the crystal particles composing the shell. The Young's modulus in the transverse section is found to have a remarkably low value.

The elastic behaviour of *Turbo* and *Trochus* in the plane of the shells is, on the other hand, isotropic agreeing well with the known randomness of crystal orientation present in these shells. In *Heliotis* (abalone) there is evidence of a definite though small elastic anisotropy, as is to be anticipated from the X-ray observations on this shell.

A general expression for calculating the elastic modulus of a compound structure in terms of the elastic moduli of component materials and their distribution is derived and by the use of this expression in combination with the observations on the Young's modulus of *M. Margaratifera*, the distribution of conchyolin in this shell is deduced. The formulæ indicate, in agreement with other evidence, that the conchyolin layers between the aragonite layers are very thin in comparison with the latter. The low value of the Young's modulus in the direction normal to the laminations as found by the experiment is also explained by the theory.

The elastic behaviour of *Nautilus Pompilius* is found to be very peculiar, showing rapid variations in the value of the Young's modulus from direction to direction in the plane of the shell. Though twinning which is known to be present in this shell, might account for this to some extent, the real cause is probably to be traced to some peculiarity in the distribution of the large amount of conchyolin present in this shell.

In conclusion, the author wishes to thank his Professor, Sir C. V. Raman, Kt., F.R.S., N.L., for helpful suggestions and kind interest in the work and for placing at the disposal of the author his valuable collection of beautiful shells.

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THE PHYSICAL IDENTITY OF ENANTIOMERS.

Part III. Viscosities, Densities and Refractivities of *d*-, *l*- and *dl*-forms of Isonitrosocamphor (Stable and Unstable), Camphor, Camphoric Acid, Camphoric Anhydride, Camphorquinone and Sodium Camphorate.

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Received May 7, 1937.

In Parts I and II of this series of investigations it has been shown that Pasteur's Law of Molecular Dissymmetry holds good rigidly as regards the magnitude of the vectorial property, namely, the rotatory dispersion. The alleged discrepancies of mandelic and camphoric acids[1] were shown to be due to slightly impure substances: when sufficient care is taken to purify them, the values of rotatory dispersion of the *dextro* and *lævo* forms are found to be identical in magnitude within the limits of experimental error (Part I).

In the present paper we have examined the *dextro* and *lævo* forms of camphor, isonitrosocamphor (stable and unstable), camphorquinone, camphoric acid, camphoric anhydride and sodium camphorate with regard to their scalar properties, *e.g.*, viscosities, densities and refractivities. The racemic forms of these compounds are also included in this study. It is clear from Tables (I to VI) and viscosity-concentration curves (Figs. 1 to 5) that the *dextro* and *lævo* forms have identical values for these properties. This, therefore, proves that Pasteur's Law of Molecular Dissymmetry also holds good rigidly for these scalar properties. The truth of Pasteur's Law of Molecular Dissymmetry is thus clearly established, both for the vectorial and the scalar properties of the substances so far examined.

The existence of racemic compounds in the liquid state has been debated for a long time. Many methods have been suggested to decide whether a racemate on fusion or solution is converted into a mixture of the opposite

[1] Campbell and Garrow, *Trans. Faraday Soc.*, 1930, **26**, 560.

and active forms or whether it retains its individuality. The study of molecular weights and absorption spectra of *d*, *l* and racemic tartaric acids in dilute solution shows no indication of the presence of the latter substance. On the other hand, measurements of colour intensity, molecular weight, density and absorption spectra in concentrated solutions lend undoubted support to the existence of racemic compound in solution. Stewart[2] found that the absorption spectra of similar solutions of *dextro* and racemic tartaric acids are identical at low concentrations, but show distinct divergence at higher concentrations (14 per cent.). Beck[3] examined the viscosities of fused mixtures of the *dextro* and *lævo* forms of camphoroxime and carvonoxime, and found that the viscosities of the antipodes of the inactive mixture were identical. These results show that in neither of these cases is any racemic compound produced : Dunstan and Thole[4] from the examination of the viscosity-concentration curves for the aqueous solutions of active and racemic tartaric acids, showed that the amount of undissociated racemic acid increases with increasing concentration. Thole[5] examined several pairs of esters of optically active and racemic acids, and obtained distinct indications of the existence of liquid racemates.

Our determinations of the viscosity of the *dextro*, *lævo* and racemic forms of the following compounds at different concentrations lend strong support to the existence of racemates in solution above certain concentrations :

(1) *Camphors* (Fig. 1, Table I).—The viscosity-concentration curves of the *dextro* and *lævo* forms are superposable for the whole range of concentration investigated. The curve for the racemic compound is indistinguishable from that of the active forms below 3·04 per cent. solution indicating that the racemic compound is completely dissociated into the optically active components. At higher concentrations, the viscosity-concentration curves of the inactive and active forms diverge more and more apart, which shows the presence of increasing amount of racemate in solution with increasing concentration.

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[2] *J. C. S.*, 1907, **91**, 1537.

[3] *Zeits. Physikal Chem.*, 1904, **48**, 670.

[4] *J. C. S.*, 1910, **97**, 1253.

[5] *Ibid.*, 1913, **103**, 25.

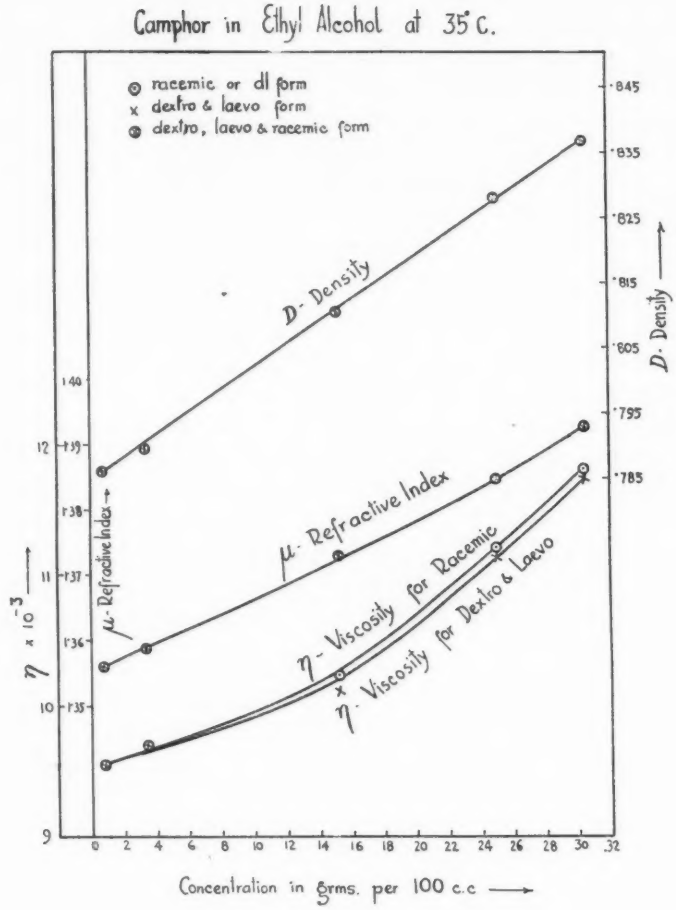
Camphor in Ethyl Alcohol at 35° C.
racemic or dl form
dextro & laevo form
dextro, laevo & racemic form
D- Density
μ- Refractive Index
η- Viscosity for Racemic
η- Viscosity for Dextro & Laevo
D- Density
μ- Refractive Index
η x 10⁻³
Concentration in grms. per 100 c.c

FIG. 1.

(2) *Isonitrosocamphors* (Fig. 2, Table II).—The viscosity-concentration curves of the stable *dextro* and *lævo* forms in ethyl alcohol are superposable but lie below that of the racemic form. Dissociation of the racemic compound is complete below 1·13 per cent. concentration, and with increase in concentration, the association into racemic aggregates increases. The *dextro* and *lævo* forms of the unstable variety give identical values for the viscosity.

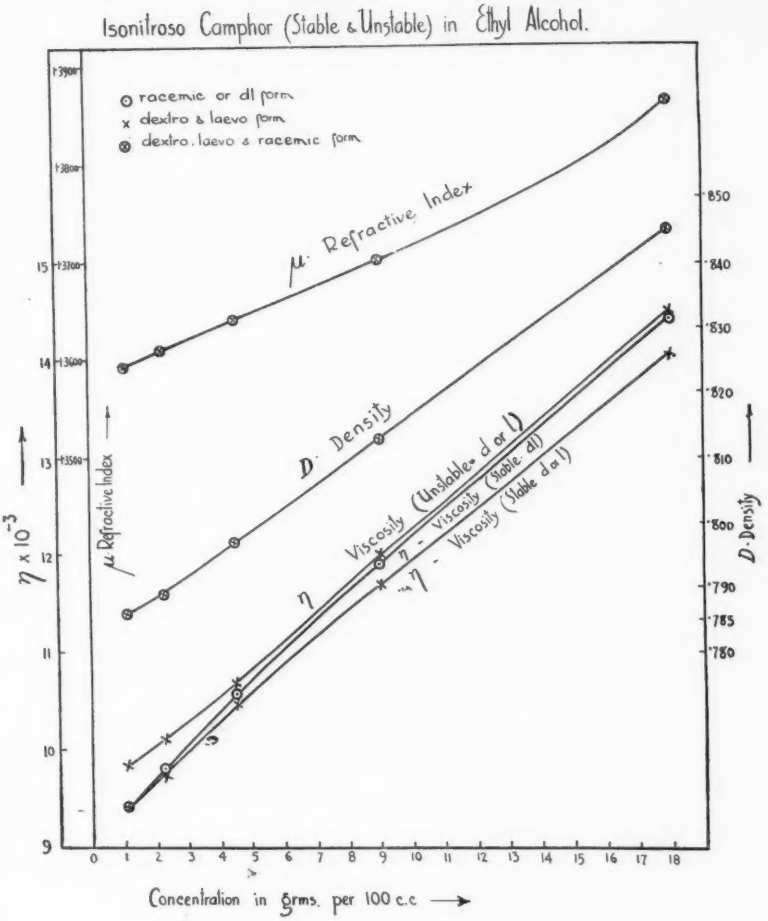
Isonitroso Camphor (Stable & Unstable) in Ethyl Alcohol.
racemic or dl form
dextro & laevo form
dextro. laevo & racemic form
μ Refractive Index
D Density
Viscosity (Unstable d or l)
η - Viscosity (Stable dl)
η - Viscosity (Stable d or l)
μ Refractive Index
D. Density
η x 10⁻³
Concentration in grms. per 100 c.c

FIG. 2.

(3) *Camphorquinones* [Fig. 3, Tables III (*a*) & (*b*)].—The dissociation of the racemic compound into the optically active components is complete below 20 per cent. solution in chloroform, as the values of the viscosity for the three forms below this concentration are identical. At concentration greater than 20 per cent. the divergence of the viscosity-concentration curves of the inactive and active forms increases, indicating the presence of increasing amount of racemate in solution. In ethyl alcohol, there is some

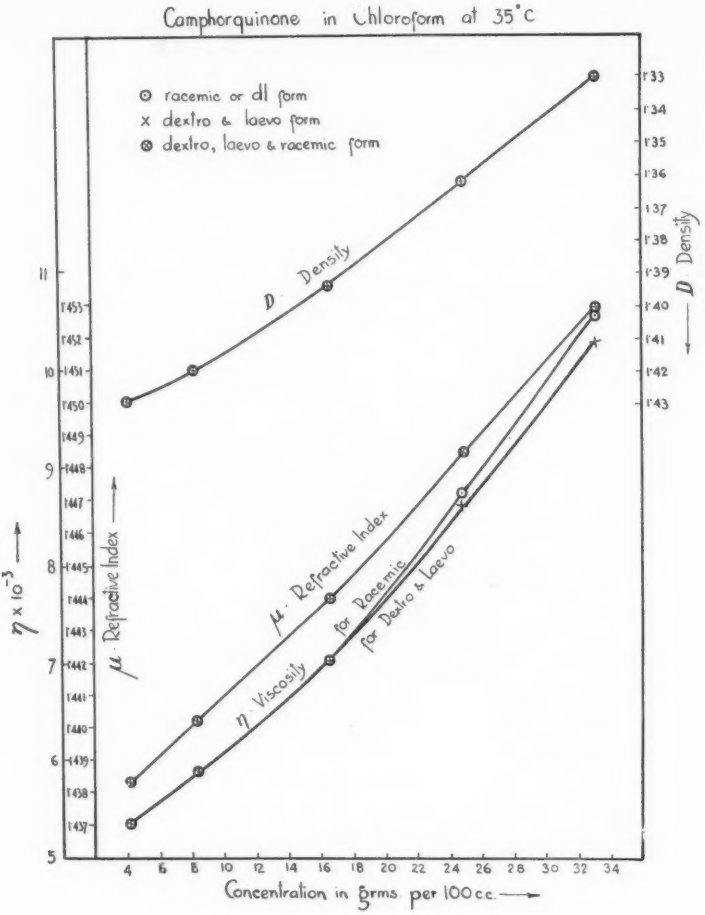
Camphorquinone in Chloroform at 35°C
racemic or dl form
dextro & laevo form
dextro, laevo & racemic form
D Density
μ Refractive Index
η Viscosity for Racemic
η Viscosity for Dextro & Laevo
η x 10⁻³
D Density
Concentration in grms per 100 cc.

FIG. 3.

indication of the existence of racemate in about 7·7 per cent. solution but below this concentration, there is complete dissociation of the racemate.

(4) *Camphoric Acids* (Fig. 4, Table IV).—The racemic form is completely dissociated below 7·5 per cent. solution in ethyl alcohol, as the three forms have identical values of viscosity below this concentration. Above this concentration, the curve of the racemic form diverges more and more from

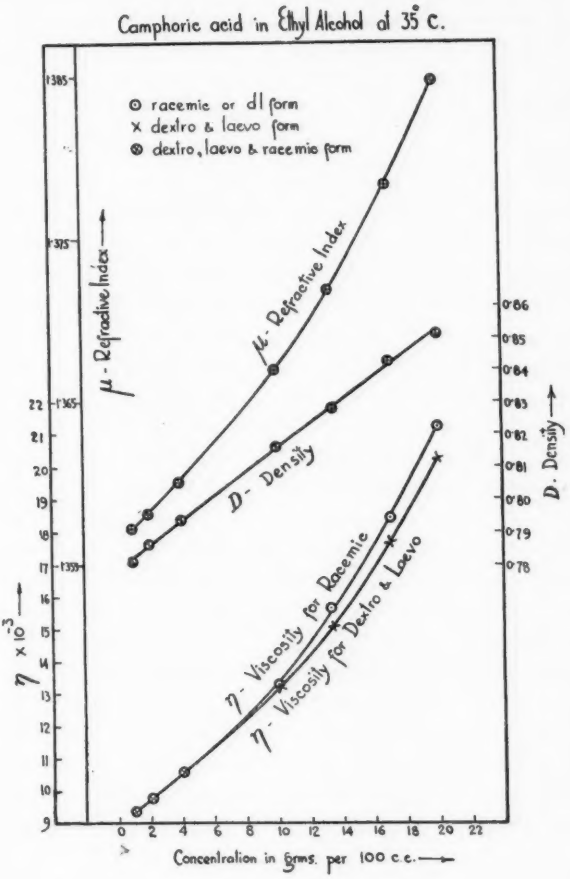
Camphoric acid in Ethyl Alcohol at 35° C.
⊙ racemic or dl form
× dextro & laevo form
⊗ dextro, laevo & racemic form
μ - Refractive Index
D - Density
η - Viscosity for Racemic
η - Viscosity for Dextro & Laevo
μ - Refractive Index
D - Density
η x 10^-3
Concentration in grms. per 100 c.c.

FIG. 4.

that of the active forms, indicating the existence of racemate at higher concentrations.

(5) *Sodium Camphorates* (Fig. 5, Table V).—The racemic form of this substance shows higher value of viscosity above 8 per cent. solution in water. There is thus very little indication of the existence of racemate in solution. The great dissociation of the racemic form of sodium camphorate in aqueous solution must be ascribed to its ionisation.

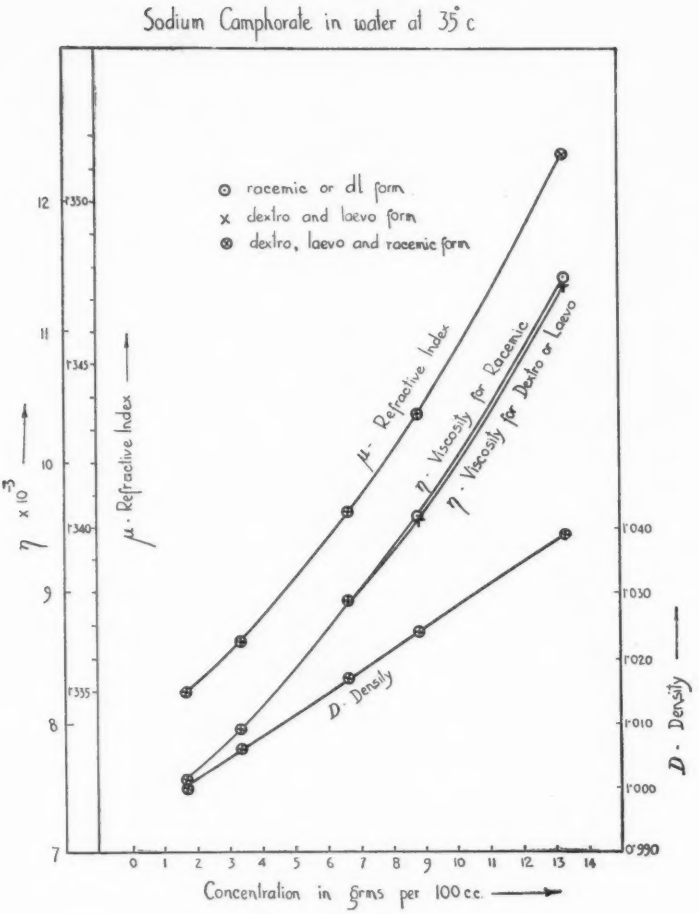
Sodium Camphorate in water at 35° c
racemic or dl form
dextro and laevo form
dextro, laevo and racemic form
μ · Refractive Index
η · Viscosity for Racemic
η · Viscosity for Dextro or Laevo
D · Density
η x 10³
μ · Refractive Index
D · Density
Concentration in grms per 100 cc.

FIG. 5.

(6) *Camphoric Anhydrides* (Table VI).—Owing to their limited solubility in ethyl alcohol, the viscosity of the three forms was determined for M/20 and M/40 solutions. At these concentrations the values of viscosity for the three forms are identical, indicating complete dissociation of the racemic form at these dilutions.

Densities.—The densities of the three forms (*d*, *l* and *dl*) of all the compounds are identical, as is evident from an examination of the Tables I to VI and Figs. 1 to 5 above referred to.

Refractivities.—The refractive index of the three forms is identical. It was, however, expected that, like the viscosity, the refractive index of the racemic form will be different from that of the active forms above certain concentrations. It is possible that this difference has not been disclosed with the Abbe Refractometer, which is not so sensitive as the Pulfrich.

Experimental.

Viscosity Determinations.—The apparatus employed for the viscosity measurements was the Ostwald modification of Poiseuille's apparatus, consisting of a fine capillary tube through which a definite volume (10 c.c.) of the solution was allowed to flow between two marks, and the time of flow carefully noted by a stop-watch to the nearest of 0·2 sec.

The viscometer was, first of all, cleaned by keeping it overnight filled with conc. nitric acid (or acid-chromate mixture). It was then washed with redistilled water (filtered), until free from acid. It was next washed with (filtered) absolute alcohol (at least thrice) and then anhydrous (filtered) ether to drive away moisture and alcohol. It was finally washed with (filtered) benzene. It was kept inverted for draining for a few minutes and then dried in a hot air oven.

The perfectly clean and dry viscometer was filled with the solution (10 c.c.) and was held firmly in a holder to fix the position of the capillary limb and immersed in a thermostat, having a glass window, the temperature of which was electrically controlled. The solution was allowed, for about an hour, to attain the temperature of the thermostat, which was previously set at 35°C. It was then sucked up to a position just above the top mark and then allowed to run freely through the capillary. The time of flow between the two marks was then measured, and several such readings were taken to ensure the concordancy of the results. Any loss or contamination of the solvent used in preparing the solution was avoided by attaching guard tubes to the limbs of the viscometer, the guard tubes having bulbs half filled with the solvent.[6] Water used for viscosity measurements as well as for solvent and washing purposes was double distilled conductivity water stored in a silica vessel.

Density Determinations.—The density was determined by means of a specific gravity bottle (glass stoppered and provided with caps). The bottle, after being thoroughly cleaned and dried, was filled with redistilled conductivity water and allowed to attain the temperature of the thermostat (35°C.) and weighed. It was again weighed in a similar manner after filling it with the solution under investigation.

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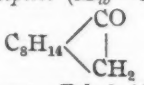
[6] Findlay, *Zeits. Physikal Chem.*, 1909, **69**, 203.

Refractive Index Determinations.—The refractive index was determined by Abbe's Refractometer in which the prism was kept at a temperature of 35°C. by circulating water from the thermostat by means of an Albany pump.

Preparation of dl-*isonitrosocamphor.*—The method of preparation of *dextro* and *lævo* isomerides has already been given in an earlier communication.[7] The two forms, stable (m.p. 152°) and unstable (m.p. 114–115°), of each isomeride were isolated. On repeating the experiment with racemic camphor only one form (m.p. 152–153°) was obtained, which we believe to be the stable form: C = 65·7, H = 8·5; $C_{10}H_{15}NO_2$ requires C = 66.3 per cent.; H = 8.28 per cent.

TABLE I.

Camphor (M_w = 152)



Solvent—Ethyl Alcohol.

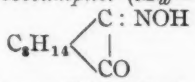
Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity* $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
2 M	dextro	310·4	600·1	0·8370	11·761	1·3930
or	lævo	310·4	600·5	0·8370	11·769	1·3930
30·4%	racemic	310·4	604·9	0·8370	11·855	1·3930
1·6447 M	dextro	310·4	575·0	0·8281	11·149	1·3850
or	lævo	310·4	574·5	0·8281	11·140	1·3850
25%	racemic	310·4	579·5	0·8281	11·236	1·3850
M	dextro	388·1	705·1	0·8034	10·609	—
or		(viscometer III)				
15·2%						
M/5	dextro	310·4	525·1	0·7895	9·707	1·3588
or	lævo	310·4	525·6	0·7895	9·716	1·3588
3·04%	racemic	310·4	524·5	0·7895	9·696	1·3588
M/20	dextro	310·4	520·0	0·7859	9·569	1·3560
or	lævo	310·4	520·4	0·7859	9·576	1·3560
0·76%	racemic	310·4	520·9	0·7859	9·586	1·3560

* In the tables, η stands for the unit of viscosity, the Poise.

[7] Singh and Prasad, *Proc. Ind. Acad. Sci.*, 1936, **3**, 586.

TABLE II.

Isonitrosocamphor (M_w = 181)

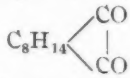


Solvent—Ethyl Alcohol.

	Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
Stable (m.p. 153–54°C.)	M	dextro	310·4	714·8	0·845	14·143	1·3868
	or	lævo	310·4	715·1	0·845	14·149	1·3868
	18·1%	racemic	310·4	733·2	0·845	14·507	1·3868
	M/2	dextro	310·4	617·9	0·813	11·763	1·3705
	or	lævo	310·4	618·1	0·813	11·766	1·3705
	9·05%	racemic	310·4	629·0	0·813	11·974	1·3705
	M/4	dextro	310·4	563·9	0·797	10·523	1·3642
	or	lævo	310·4	564·0	0·797	10·525	1·3642
	4·525%	racemic	310·4	571·2	0·797	10·660	1·3642
	M/8	dextro	310·4	538·8	0·789	9·954	1·3610
	or	lævo	310·4	538·2	0·789	9·943	1·3610
	2·2625%	racemic	310·4	541·2	0·789	9·998	1·3610
	M/16	dextro	310·4	514·8	0·786	9·474	1·3592
	or	lævo	310·4	515·0	0·786	9·478	1·3593
	1·1312%	racemic	310·4	515·2	0·786	9·482	1·3593
Unstable (m.p. 114–15°C.)	M	dextro	310·4	737·4	0·845	14·590	1·3869
	or	lævo	310·4	737·6	0·845	14·594	1·3868
	18·1%						
	M/2	dextro	310·4	634·7	0·813	12·082	1·3705
	or	lævo	310·4	634·9	0·813	12·086	1·3706
	9·05%						
	M/4	dextro	310·4	575·5	0·797	10·740	1·3642
	or	lævo	310·4	575·8	0·797	10·745	1·3642
	4·525%						
	M/8	dextro	310·4	548·2	0·788	10·115	1·3610
	or	lævo	310·4	548·7	0·789	10·137	1·3612
	2·2625%						
	M/16	dextro	310·4	538·1	0·785	9·891	1·3596
	or	lævo	310·4	538·4	0·785	9·896	1·3594
	1·1312%						

TABLE III (*a*).

Camphorquinone ($M_w = 166$)

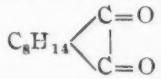


Solvent—Chloroform.

Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
2 M	dextro	310·4	331·5	1·330	10·324	1·4530
or	lævo	310·4	330·5	1·330	10·292	1·4530
33·2%	racemic	310·4	338·7	1·330	10·548	1·4530
		(viscometer I)				
1·5 M	dextro	310·4	270·4	1·362	8·623	1·4485
or	lævo	310·4	269·9	1·362	8·607	1·4485
24·9%	racemic	310·4	274·4	1·362	8·751	1·4485
		(viscometer I)				
M	dextro	225·4	156·3	1·394	7·026	1·4440
or	lævo	225·4	156·4	1·394	7·030	1·4440
16·6%	racemic	225·4	156·4	1·394	7·030	1·4438
		(viscometer II)				
M/2	dextro	225·5	128·2	1·420	5·870	1·4402
or	lævo	225·4	128·2	1·420	5·870	1·4402
8·3%	racemic	225·4	128·4	1·420	5·879	1·4402
		(viscometer II)				
M/4	dextro	310·4	160·1	1·430	5·361	1·4383
or	lævo	310·4	160·2	1·430	5·364	1·4383
4·15%	racemic	310·4	161·2	1·430	5·398	1·4383
		(viscometer I)				

TABLE III (*b*).

Camphorquinone ($M_w = 166$)



Solvent—Ethyl Alcohol.

Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
0·466 M	dextro	225·4	382·2	0·8002	9·862	1·3648
or	lævo	225·4	382·5	0·8001	9·868	1·3648
7·742%	racemic	225·4	384·2	0·8007	9·920	1·3648
M/4	dextro	225·4	376·6	0·7904	9·598	1·3606
or	lævo	225·4	376·1	0·7903	9·584	1·3606
4·15%	racemic	225·4	375·1	0·7907	9·564	1·3608
M/10	dextro	225·4	372·5	0·7833	9·409	1·3572
or	lævo	225·4	372·4	0·7833	9·406	1·3572
1·66%	racemic	225·4	372·8	0·7834	9·417	1·3572

TABLE IV.

Camphoric Acid (M_w=200)

C_8H_{11}(COOH, COOH)

Solvent—Ethyl Alcohol.

Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
M	dextro	310·4	1017·4	0·8513	20·280	1·3847
or	lævo	310·4	1018·3	0·8513	20·298	1·3847
20%	racemic	310·4	1061·0	0·8513	21·149	1·3850
0·85 M	dextro	310·4	898·4	0·8425	17·722	1·3784
or	lævo	310·4	898·8	0·8425	17·730	1·3784
17·0%	racemic	310·4	935·4	0·8425	18·453	1·3784
2/3 M	dextro	310·4	782·1	0·8275	15·154	1·3720
or	lævo	310·4	782·4	0·8275	15·160	1·3720
13·33%	racemic	310·4	808·5	0·8275	15·665	1·3720
M/2	dextro	310·4	694·2	0·8154	13·254	1·3670
or	lævo	310·4	693·9	0·8156	13·252	1·3670
10%	racemic	310·4	698·2	0·8156	13·334	1·3670
M/5	dextro	310·4	567·1	0·7935	10·536	1·3602
or	lævo	310·4	566·6	0·7935	10·527	1·3602
4%	racemic	310·4	568·0	0·7935	10·553	1·3602
M/10	dextro	310·4	533·4	0·7860	9·817	1·3581
or	lævo	310·4	533·4	0·7860	9·817	1·3581
2%	racemic	310·4	533·6	0·7860	9·820	1·3581
M/20	dextro	310·4	513·4	0·7811	9·390	1·3572
or	lævo	310·4	513·2	0·7811	9·386	1·3572
1%	racemic	310·4	512·8	0·7811	9·379	1·3572

TABLE V.

Sodium Camphorate (M_w = 334)

$$C_8H_{14}\begin{matrix}COONa\\ \\ COONa\end{matrix}\cdot 5H_2O$$

Solvent—Water.

Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
0·4 M	dextro	310·4	467·4	1·0390	11·361	1·3515
or	lævo	310·4	467·8	1·0390	11·371	1·3515
13·36%	racemic	310·4	469·9	1·0389	11·431	1·3515
0·265 M	dextro	310·4	399·4	1·0240	9·576	1·3435
or	lævo	310·4	399·3	1·0240	9·574	1·3435
8·84%	racemic	310·4	399·8	1·0239	9·585	1·3435
0·2 M	dextro	310·4	375·9	1·0170	8·951	1·3405
or	lævo	310·4	376·2	1·0169	8·958	1·3405
6·68%	racemic	310·4	375·4	1·0170	8·939	1·3405
0·1 M	dextro	310·4	338·5	1·0060	7·974	1·3365
or	lævo	310·4	338·6	1·0060	7·976	1·3365
3·34%	racemic	310·4	338·2	1·0062	7·968	1·3365
0·05 M	dextro	310·4	323·2	0·9999	7·567	1·3350
or	lævo	310·4	323·5	0·9998	7·573	1·3350
1·67%	racemic	310·4	324·4	0·9998	7·594	1·3350

TABLE VI.

Camphoric Anhydride (M_w = 182)

$$C_8H_{14}\begin{matrix}CO\\ \\ CO\end{matrix}\!\!>O$$

Solvent—Ethyl Alcohol.

Concentration g/100 c.c.	Isomeride	Time of flow for water in seconds	Time of flow for solution in secs.	Density $[D]^{35°}$	Viscosity $[\eta \times 10^{-3}]^{35°}$	Refractive Index $[n]^{35°}$
M/20	dextro	310·4	502·5	0·7809	9·188	1·3572
or	lævo	310·4	502·7	0·7809	9·192	1·3572
0·64%	racemic	310·4	502·7	0·7809	9·192	1·3572
M/40	dextro	310·4	500·9	0·7799	9·147	1·3560
or	lævo	310·4	500·6	0·7799	9·142	1·3560
0·32%	racemic	310·4	500·8	0·7799	9·145	1·3560

Summary.

1. The viscosities, densities and refractivities of the *dextro* and *lævo* isomerides are identical: the composition curves for these functions for the two forms are superposable.

2. The densities of the racemic and optically active forms are identical.

3. The plot of density against composition in all cases except one is a straight line. The linear relationship does not hold for solutions of camphoquinone in chloroform indicating that the change of volume on solution is not uniform throughout the range of concentrations investigated.

4. There is undoubted evidence of the existence of racemates in solution in all cases. The viscosity-concentration curves show that the amount of the undissociated racemic form increases with concentration. As the concentration is decreased, a point is reached (which varies with different compounds), below which all the three forms (*d*, *l* and *dl*) of a substance give identical values for viscosity, indicating complete dissociation of the racemate in solution. In the case of *dl*-camphoric acid in ethyl alcohol, the limit is reached in about 2 per cent. solution, whereas in the case of *dl*-camphorquinone, this point is reached in about 18 per cent. solution in chloroform, and in about 5 per cent. solution in ethyl alcohol. At these concentrations, the viscosity concentration curves of the racemic and optically active forms show distinct divergence, which increases with concentration, the racemic form having higher viscosity.

5. The refractivity of the racemic and the optically active forms is identical for all concentrations. As pointed out above, the differences at higher concentrations are not disclosed by the Abbe Refractometer.

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